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[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON THE BEHAVIOR OF TRIETHYLAMINE TOWARDS OXIDIZING AGENTS.

By T. Dar Juan.

It has long been known that ammonia can be converted, by treatment with ethyl halides, ethyl sulphate or ethyl nitrate, into a mixture of ethylated ammonium salts. According to Nef's interpretation,[1] this reaction takes place because of a union of ethylidene with ammonia,

$$CH_3.CH \Big< \ + H—NH_2 \rightleftarrows CH_3—CH_2—NH_2, \text{ etc.};$$
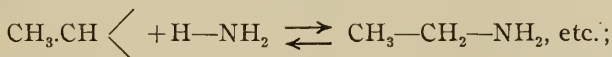
furthermore, many facts show very decisively that Hofmann's reaction is reversible. We can, for example, convert tetra-ethylammonium chloride, by means of an excess of dry hydrogen chloride, quantitatively at 300° into ammonium chloride and four molecules of ethyl chloride,

$$(C_2H_5)_4NCl + 4HCl \longrightarrow 4C_2H_5Cl + NH_4Cl.$$
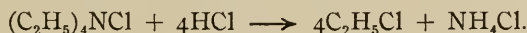
The remarkable fact that dry ethylammonium chloride gives at 300° one molecule of ethyl chloride and ammonia,

$$C_2H_5NH_3Cl \longrightarrow C_2H_5Cl + NH_3,$$
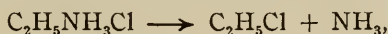
[1] Ann. Chem. (Liebig), **309**, 160–3; **318**, 2.

whereas with a soluble alkaline hydroxide, at ordinary temperature, it gives ethylamine and a metallic chloride,

$$C_2H_5NH_3Cl + KOH \longrightarrow C_2H_5NH_2 + KCl + H_2O,$$

must, in the light of Nef's work, be interpreted as follows:

The normal products of dissociation of the salt named are ethylamine and hydrogen chloride,

$$C_2H_5NH_3Cl \rightleftarrows C_2H_5NH_2 + HCl,$$
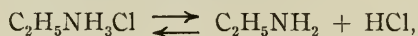
but ethylamine is itself in turn considerably dissociated at 300° into ethylidene and ammonia,

$$C_2H_5NH_2 \rightleftarrows CH_3CH + NH_3;$$
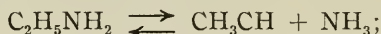
consequently ethylidene unites with the hydrogen chloride present to give the far more stable and less dissociated ethyl chloride. The decomposition of dry ethylammonium chloride at 300° accordingly takes place in two successive steps,[1]

$$C_2H_5NH_3Cl \rightleftarrows C_2H_5NH_2 + HCl \longrightarrow$$
$$C_2H_4 + NH_3 + HCl \longrightarrow C_2H_5Cl + NH_3.$$
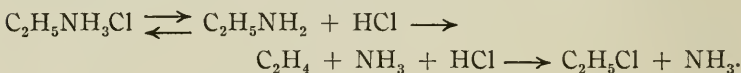
An entirely analogous interpretation obviously holds for the transformation referred to above of tetraethylammonium chloride into ethyl and ammonium chlorides by dry hydrogen chloride.

It was now also possible, in the light of these new views, for me to begin, under Dr. Nef's guidance and direction, a systematic study of the behavior of the substituted ammonias towards oxidizing agents.

There are two ways, theoretically, in which an oxidizing agent may act upon triethylamine, for example; first, the active molecules of this substance may unite directly with oxygen to give the oxide,

$$(\text{I})\quad (C_2H_5)_3N\!\!\big\langle \;+\; 2(OH) \longrightarrow (C_2H_5)_3N(OH)_2 \longrightarrow$$
$$(C_2H_5)_3N{=}O + H_2O,$$
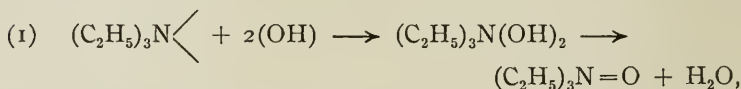
which must then be further oxidized to nitric and acetic acids; second, only the ethylidene molecules, present in very small concentration at ordinary temperature in triethylamine,

[1] Ann. Chem. (Liebig), **309**, 163.

(2) $(C_2H_5)_3N \rightleftarrows C_2H_4 + NH(C_2H_5)_2 \rightleftarrows$
$$2C_2H_4 + NH_2C_2H_5 \rightleftarrows 3C_2H_4 + NH_3,$$
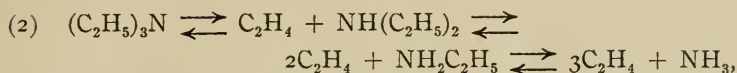
may act with the oxidizing agent present to give acetalde-
hyde and the products of its further oxidation, leaving there-
fore free ammonia as such. Assuming for a moment that
the oxidation could be carried out so that the ammonia set
free according to (2) remains unaltered, it would then ob-
viously be possible to determine exactly the percentage of
oxidation proceeding according to (1) and (2), respectively.

Now we know from qualitative and preliminary experi-
ments of Carstanjen,[1] as well as of Claisen and Wallach,[2]
that the ethylated ammonias give in the cold, with aqueous
potassium permanganate, large amounts of acetic acid as well
as free ammonia, indicating therefore that the oxidation ac-
cording to (2) must be the chief one. I have therefore re-
peated these experiments with great care and have deter-
mined quantitatively the amounts of acetic, carbonic, oxalic
and nitric acids, as well as of ammonia, which are formed
under various conditions, from known amounts of triethyl-
amine and permanganate, at 20° to 100°. Since, however,
recent experiments by Herschkowitsch[3] show that ammonia
itself is slowly converted by alkaline or aqueous potassium
permanganate into nitrogen, as well as into nitric acid, my
results prove only that the main oxidation of triethylamine
proceeds according to (2); they are as yet inadequate in en-
abling us to decide what percentage of the oxidation (if any)
proceeds according to reaction (1).

The carbon atoms in triethylamine are converted quantita-
tively into three molecules of acetic acid when aqueous per-
manganate only is used; if, however, potassium hydroxide
is also simultaneously present, carbonic and oxalic acids also
appear (in large amounts, the greater the concentration of
the alkali) besides acetic acid. This result is self-evident
in view of the recent work of Miss Denis,[4] who has proved that

[1] J. prakt. Chem., **89,** 486.
[2] Ber. d. chem. Ges., **8,** 1237.
[3] Z. physik. Chem., **65,** 93.
[4] THIS JOURNAL, **38,** 561.

acetaldehyde, formed through the oxidation of ethylidene (in ether and alcohol), gives large amounts of carbonic and oxalic acids when oxidized with alkaline permanganate, owing to an intermediate formation and oxidation of vinyl alcohol and diose.

Triethylamine and Permanganate.—An aqueous solution containing 3 grams of triethylamine was treated with 593 cc. normal potassium permanganate solution. Complete decolorization took place after standing twenty-four hours in the cold; small amounts of permanganate were now added and the solution was finally heated in a bath kept at 100° and under a reflux condenser which was connected with a receiver containing hydrogen chloride to prevent loss of ammonia. It was found that a total of 808 cc. permanganate solution was needed before the solution finally became practically decolorized on long boiling. A known quantity of potassium hydroxide was now added and the ammonia present in the aqueous solution was then driven out by hard boiling (in a bath kept at 120°) and collected in a receiver containing an excess of hydrogen chloride. The weight of ammonium chloride obtained on evaporating the acid solution on a water bath was 0.8 gram, which is 50.4 per cent. of the calculated amount; the salt obtained was proved to be free from traces of ethylated ammonium chlorides, as it sublimed without melting and gave, on digestion with alcohol, no easily soluble and low-melting salts.

The original alkaline solution was then filtered from the insoluble manganese dioxide and treated with the calculated amount of hydrogen chloride. The carbon dioxide thus set free was then determined quantitatively in the usual manner by expulsion and absorption in an aqueous solution of barium hydroxide.[1] The aqueous distillates (free from hydrochloric acid), on removal of water and volatile acids by fractionating at reduced pressure and heating finally up to 100°, were found to contain both nitric and acetic acids; after titrating an aliquot portion with 0.1 N potassium hydroxide solution the main portion of the distillate was neturalized with caustic

[1] THIS JOURNAL, **38**, 561.

potash. Since potassium acetate is easily soluble in cold absolute alcohol and potassium nitrate practically insoluble in this solvent, a separation of the two salts could easily be accomplished; the potassium acetate was then converted into silver acetate which was analyzed. Thorough extraction with ether of the original salt residue gave finally, after removal of the volatile acids by distillation as stated, any oxalic acid formed in the oxidation process.

The total volume of aqueous distillate was 2 liters; 100 cc. of this required 38.2 cc. 0.1 N potassium hydroxide solution for neutralization; treatment of the remainder with 0.1 N caustic potash, etc., gave a total of 6.9 grams potassium salt (acetate) soluble in alcohol and 0.65 gram potassium nitrate; the former salt, treated in aqueous solution with silver nitrate, gave 10.5 grams of crystallized silver acetate, corresponding to 6.165 grams potassium acetate, or 3.775 grams acetic acid, *i. e.*, 70.7 per cent. of the amount theoretically possible.

0.3107 gram salt gave, on ignition, 0.2005 gram Ag.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.52

No trace of oxalic or of carbonic acid was obtained in the experiment.

Triethylamine and Alkaline Permanganate.—Two experiments were carried out with 10 and 20 molecules of potassium hydroxide, respectively. In the first one a mixture of 4 grams triethylamine and 22 grams potassium hydroxide, in a small amount of water, was treated with one liter of normal potassium permanganate solution; it was found necessary to add 0.15 gram more triethylamine in order to entirely decolorize the permanganate on the boiling water bath. The amount of ammonium chloride obtained was 1.8 grams, or 82 per cent. of the calculated amount; 1.2 grams of crystallized oxalic acid melting from 99°–100° or, after loss of water of crystallization, from 186°–187°, and 1.181 gram carbon dioxide were formed from the 4.15 grams of triethylamine.

The volume of the aqueous distillate was 2.5 liters; 100

cc. required 35.4 cc. 0.1 N caustic potash for neutralization; the total amount of potassium nitrate obtained was 0.46 gram; the potassium acetate 9.83 grams, giving, by double decomposition, 14 grams of crystallized silver acetate, corresponding to 5.032 grams of acetic acid.

0.2532 gram of the silver acetate gave, on ignition, 0.1637 gram Ag.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.66

In the second experiment, where 4 grams of triethylamine, 44 grams of potassium hydroxide and 1 liter of permanganate solution were used, decolorization took place after standing 8 hours in the cold; it was finally found necessary to add 260 cc. more of the oxidizing agent to complete the reaction at 100°. The amount of ammonium chloride obtained was 1.72 grams, or 81.3 per cent.; carbon dioxide, 2.418 grams; crystallized oxalic acid, 1.6 grams. The aqueous distillate (volume 2.500 cc., 100 cc. requiring 31.24 cc. 0.1 N potassium hydroxide solution) gave, on neutralization, 0.44 gram of potassium nitrate and 8.2 grams potassium acetate, which was converted in the usual manner into 12.22 grams crystallized silver acetate corresponding to 4.39 grams acetic acid.

It will be noticed that decidedly more ammonia, over 80 per cent. of the calculated amount, is formed when caustic alkali is present as well as the oxidizing agent; that carbon dioxide and oxalic acid also appear under these conditions, thus diminishing the amount of acetic acid formed, which is, however, still the main oxidation product. Finally, it should be stated here that no experiments were carried out with mono- and diethylamine, which are evidently intermediate products in the conversion of triethylamine into acetic acid and ammonia by neutral permanganate. Strangely enough, however, it was found that tetraethylammonium hydroxide is not perceptibly oxidized by long boiling either with neutral or alkaline permanganate solution.

The writer wishes to express his thanks to Professor Nef for his guidance and direction in this work.

[Contribution from the Chemical Laboratory of Harvard College.]

ON THE ACTION OF ACETIC ANHYDRIDE ON THE OCTOBROMORTHOQUINO-1-METHOXY-1'-HY-DROXY-1-PHENYLENE MONOXIDE.

By C. Loring Jackson and H. A. Flint.

Many experiments have been tried in this laboratory on the action of acetic anhydride with the α-bodies, octobrom-o-quino-1-alkoxy-1'-hydroxy-1-phenylene monoxide,

$$C_6Br_4O(OR)-O-(HO)OC_6Br_4$$
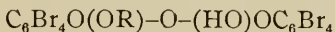
(in which R represents the alkyl radical), made by allowing an alcohol to stand with the tetrabrom-o-benzoquinone in the cold. Special attention has been given to these reactions because in the earliest work[1] on this subject it was found that the α-benzyl compound, when warmed for a short time from 60° to 70° with acetic anhydride, was converted into the β-compound, octobrom-1-benzyloxy-1'-hydroxy-1,2,2-phenylene trioxide,

$$C_6Br_4(OC_7H_7)O_3(HO)C_6Br_4,$$
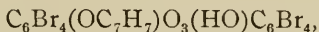
and the hexabrom-o-quinopyrocatechin ether,

$$C_6Br_4O_2C_6Br_2O_2;$$
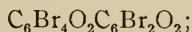
and this reaction was used later[2] in determining the constitution of the α- and β-compounds. In the earlier experiments the β-benzyl compound, when boiled with acetic anhydride for 4 or 5 hours, was decomposed instead of giving the expected acet compound, but afterward H. A. Carlton and one of us[3] succeeded in preparing this acet derivative by boiling the β-compound with acetic anhydride for only 15 minutes, whereas, if the boiling was continued for 6 hours, a charred mass was formed, from which only a few brown needles could be extracted.

Finally, in the paper in which the constitution of the α- and β-compounds was worked out, R. D. MacLaurin and one

[1] Jackson and Porter: This Journal, **31**, 103 (1904).
[2] Jackson and MacLaurin: Ibid., **37**, 92 (1907).
[3] Ibid., **34**, 440 (1905).

of us described some preliminary experiments[1] on the action of acetic anhydride in the cold on the α-methyl compound, which yielded after several hours a yellow substance melting at 225° and a white one melting at 218°. No work was done on the latter, but the yellow product contained an amount of bromine corresponding to that in the α-body, and, as it seemed to be a definite compound, it was suggested that it might belong to a third (γ) class. With warm acetic anhydride Dr. MacLaurin obtained products melting at 138°–140° and at 195° with the hexabrom-*o*-quinopyrocatechin ether.

These earlier experiments gave results which invited further study, and in this paper we describe an investigation of Dr. MacLaurin's yellow product. This we prepared by allowing the acetic anhydride to act on the α-body for a week or 10 days instead of a few hours. The product obtained under these conditions showed the constant melting point 244° instead of 225°, as observed by Dr. MacLaurin in his preliminary experiments. This difference in the two results is not hard to understand; the melting is accompanied by decomposition, and in these cases the temperature is much influenced by the conditions of heating, so that constant results can be obtained only when these conditions are the same, and two different observers might well find melting points many degrees apart, showing a difference even as large at 19°. It is also possible that the product of Dr. MacLaurin's preliminary experiments contained a persistent impurity of the unchanged α-compound, and this supposition is in harmony with the fact that he allowed the action of the acetic anhydride to proceed only for a few hours, whereas we found at least a week was necessary to complete it.

The melting point 244° suggested at once that the substance was the heptabrom-*o*-quinopyrocatechin hemiether,

$$C_6Br_4(OH)OC_6Br_3O_2,$$
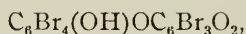
and this was proved to be the case by its analysis and its other properties. This substance oddly enough contains the same amount of bromine as the α-methyl compound, but the de-

terminations of carbon and hydrogen proved that it has a different composition. The formation of the heptabrom hemiether would indicate that the acetic anhydride had decomposed the α-body completely into two molecules of tetrabrom-*o*-quinone and methyl alcohol (or more probably acetate), and that one of these quinones had then undergone a reduction to tetrabrompyrocatechin, which afterward combined with the remaining quinone with loss of hydrobromic acid. The hexabrom-*o*-quinopyrocatechin ether obtained by Dr. Porter from the α-benzyl compound and hot acetic anhydride must have been formed in a similar way. It is certainly strange that compounds so stable as these toward other reagents should be decomposed by acetic anhydride, but as stated earlier the fact has been observed repeatedly in this laboratory.

In our experiments, which were carried on for a longer time than Dr. MacLaurin's, none of his white product was obtained so we are unable to give any account of this body, and our experiments with warm acetic anhydride apparently ran beyond the low-melting products found by him, as we obtained the heptabrom hemiether, $C_6Br_4(OH)OC_6Br_3O_2$, and the hexabrom ether, $C_6Br_4O_2C_6Br_2O_2$.

The further study of the reactions of acetic anhydride with the α-bodies will be carried on in this laboratory.

<div align="center">EXPERIMENTAL.</div>

The tetrabrom-*o*-benzoquinone used was prepared by the method described by us in a previous paper.[1] The method[2] for preparing the α-compound was improved by putting the mixture of 50 grams of tetrabrom-*o*-quinone and 100 cc. of methyl alcohol in a glass-stoppered bottle on the shaking machine, when the reaction was complete in six or seven days, thus saving from one-third to one-half the time required when the mixture was allowed to stand at rest as in the earlier method.

Ten grams of the α-compound, $(C_6Br_4O_2)_2CH_3OH$, mixed with 80 cc. of acetic anhydride, were shaken for 15 minutes

[1] THIS JOURNAL, **39**, 83 (1908).
[2] Jackson and Porter: *Ibid.*, **31**, 95 (1904). Jackson and Carlton: *Ibid.*, **34**, 425 (1905).

and then allowed to stand with only occasional shaking at ordinary temperatures for a week or 10 days, that is, until the white color of the original substance had been completely replaced by yellow. The product was then filtered out, washed with gasoline, and recrystallized from a mixture of benzene and gasoline, until it showed the constant melting point 244°, when it was dried *in vacuo* for analysis:

I. 0.2172 gram substance gave 0.1466 gram CO_2 and 0.0077 gram H_2O.

II. 0.3762 gram substance gave 0.2650 gram CO_2 and 0.0142 gram H_2O.

III. 0.1432 gram substance gave 0.2452 gram AgBr.

IV. 0.1456 gram substance gave 0.2496 gram AgBr.

V. 0.1515 gram substance gave 0.2585 gram AgBr.

	Calculated for $C_6Br_4OHOC_6Br_3O_2$.	I.	II.	Found. III.	IV.	V.
C	18.73	18.41	19.21	...	...	...
H	0.13	0.39	0.42	...	...	...
Br	72.81	...	...	72.86	72.97	72.63

The substance is therefore the heptabrom-*o*-quinopyrocatechin hemiether, and this is confirmed by its melting at 244° with the formation of a red liquid, and the fact that, when crystallized from a solvent containing benzene, it appears in the very characteristic square plates of a brilliant yellow color, which effloresce on exposure to the air. Warm alcohol converts it into the hexabrom-*o*-quinopyrocatechin ether, and its solubilities are the same as those of the heptabrom compound.

To study the action of hot acetic anhydride 2 grams of the α-body were dissolved in 30 cc. of acetic anhydride and warmed on the steam bath for half an hour, after which the addition of 500 cc. of water precipitated a pale reddish substance. Ether extracted from this a quantity of the heptabrom-*o*-quinopyrocatechin hemiether, identified by its melting point and properties, and left behind a red body, which did not melt below 300°, was essentially insoluble in all the common solvents, but could be crystallized from nitrobenzene, and was therefore undoubtedly the hexabrom-*o*-quinopyrocatechin

ether, $C_6Br_4O_2C_6Br_2O_2$. The acetic anhydride in this experiment behaved in the same way as it did when acting in the cold, the hexabrom compound being undoubtedly formed from the heptabrom hemiether, which was the first product.

In a preliminary experiment a few grams of heptabrom-*o*-quinopyrocatechin hemiether were shaken for 8 hours with a 10 per cent. solution of sodic hydrate. The product formed white rhombic crystals and melted with decomposition at about 240°. It was remarkable, because it gave so faint a test for halogen on copper wire that it seemed to be free from bromine. It will be investigated further.

CAMBRIDGE, October 27, 1909.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXVI.—RESEARCHES ON HALOGENAMINO ACIDS: THE POSITION OF THE IODINE ATOMS IN DI-IODTYROSINE (IODGORGOIC ACID).

[EIGHTH PAPER.]

By HENRY L. WHEELER AND CARL O. JOHNS.

Diiodtyrosine was first prepared synthetically by Wheeler and Jamieson.[1] Our work at that time served to show that this substance is identical with iodgorgoic acid, which Drechsel[2] obtained by the hydrolysis of a Mediterranean coral (*Gorgonia Cavolini*).

It has not hitherto been determined in what part of the molecule the iodine atoms are located. From the fact that halogens attack phenols in the ortho, in preference to the meta positions, we suggested that the compound was 3,5-diiodtyrosine. Since then this substance has been referred to by various writers as 3,5- and also, without adequate reason, as 2,5-diiodtyrosine.

In this paper we describe the results of our work, which now conclusively prove that the iodine atoms in diiodtyrosine are attached in the 3- and 5-positions. It has been found by Dr.

[1] THIS JOURNAL, **33**, 365 (1905)
[2] Z. Biol., **33**, 90 (1896).

S. H. Clapp, working with one of us, that diiodtyrosine can easily be methylated by means of methyl iodide and potassium hydroxide. When this methylated product, which is provisionally[1] represented by formula II, was boiled with sodium hydroxide a sodium salt of an acid free from nitrogen was obtained. This acid, moreover, contained iodine and, on analysis, gave results agreeing with those calculated for a diiod-*p*-methoxycinnamic acid (III).

A similar behavior has apparently been observed in the case of tyrosine. Körner and Menozzi[2] found, on methylating tyrosine, that a compound represented by the formula

$$CH_3OC_6H_4C_2H_3(CO_2K)N(CH_3)_3I,$$
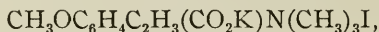
was obtained. When this was warmed with alkali *p*-cumaric acid was formed. This paper is inaccessible to us at present. We have now prepared 3,5-diiod-*p*-methoxycinnamic acid (III) from material which has been proved by us to have the halogen in the 3- and 5-positions and we find that this synthetic preparation and that obtained from diiodtyrosine by degradation (*Abbau*) are identical. 3,5-Diiod-*p*-methoxycinnamic acid (III) was prepared by methylating the diiod-*p*-hydroxycinnamic acid (V) of Paal and Mohr.[3] This process gave a mixture of the acid (III) and the methyl ester (IV).

The diiod-*p*-hydroxycinnamic acid was prepared from diiod-*p*-hydroxybenzaldehyde (VI), which, in turn, was obtained by iodating *p*-hydroxybenzaldehyde as described by Paal.[4] Paal and Mohr state that by oxidizing this diiod aldehyde the *m*-diiod-*p*-hydroxybenzoic acid (VII) of Peltzer[5] smoothly results and that therefore the constitution is established.

A search through Peltzer's article failed to reveal any proof or mention whatever of the position of the halogen in his acid. In fact he tried to determine the structure of the acid by heating with soda, in the hope of obtaining gallic acid or an isomer.

[1] Owing to the departure of Dr. Clapp before the work was finished, a description of the methylated product is reserved for a later paper.

[2] Gazz. Chim. Ital., **11**, 550; Beilstein's Handbuch, [3] **2**, 1569.

[3] Ber. d. chem. Ges., **29**, 2306 (1896).

[4] *Ibid.*, **28**, 2412 (1895).

[5] Ann. Chem. (Liebig), **146**, 294 (1868).

His attempts were, however, unsuccessful. No other work on this acid being known to us, it was necessary to establish the structure of this compound.

The proof that the iodine atoms are in the 3,5-positions in diiod-*p*-hydroxybenzoic acid was obtained by Wheeler and Liddle[1] by converting the 3,5-diiod-*p*-aminobenzoic acid (VIII) into the hydroxy acid in question. This acid was first prepared by Michael and Norton.[2] They did not prove, but, here again, assumed as most probable, that the iodine atoms were in the 3,5-positions.

This diiodamino acid (VIII), however, has been shown by Wheeler and Liddle to be a 3,5-diiod derivative. Its structure was established in two different ways.

In the first case it was obtained by oxidizing the acetyl derivative of 3,5-diiod-*p*-toluidine (XI) which, on diazotizing and removing the amino group, gave 3,5-diiodtoluene (XII). In the second case the diiodamino acid was converted by the diazo reaction into a diiodbenzoic acid (IX), which was found to be identical with 3,5-diiodbenzoic acid prepared from Hübner's 3,5-dinitrobenzoic acid (XIII). The nitro groups in the latter compound were alternately reduced and replaced by iodine. In this manner we obtained 3-nitro-5-aminobenzoic acid (XIV), 3-nitro-5-iodbenzoic acid (XV), 3-amino-5-iodbenzoic acid (X), and finally 3,5-diiodbenzoic acid (IX).

These results settle the structure of diiodtyrosine. They also settle the structure of the other compounds which were previously assumed to be 3,5-diiod derivatives. The formulas and the relations of the substances may be represented as follows:

[1] This Journal, **42**, 441 (1909).
[2] *Ibid.*, **1**, 264 (1879).

$CH_2CH(NH_2)COOH$ $CH_2CH(N(CH_3)_3I)COOH$ $CH=CHCOOH$

I.

II.

III.

$CH=CHCOOCH_3$

IV.

$CH=CHCOOH$

V.

CHO

VI.

COOH

VII.

COOH

VIII.

COOH

IX.

CH_3

XII.

CH_3

XI.

COOH

X.

COOH

XIII.

COOH

XIV.

COOH

XV.
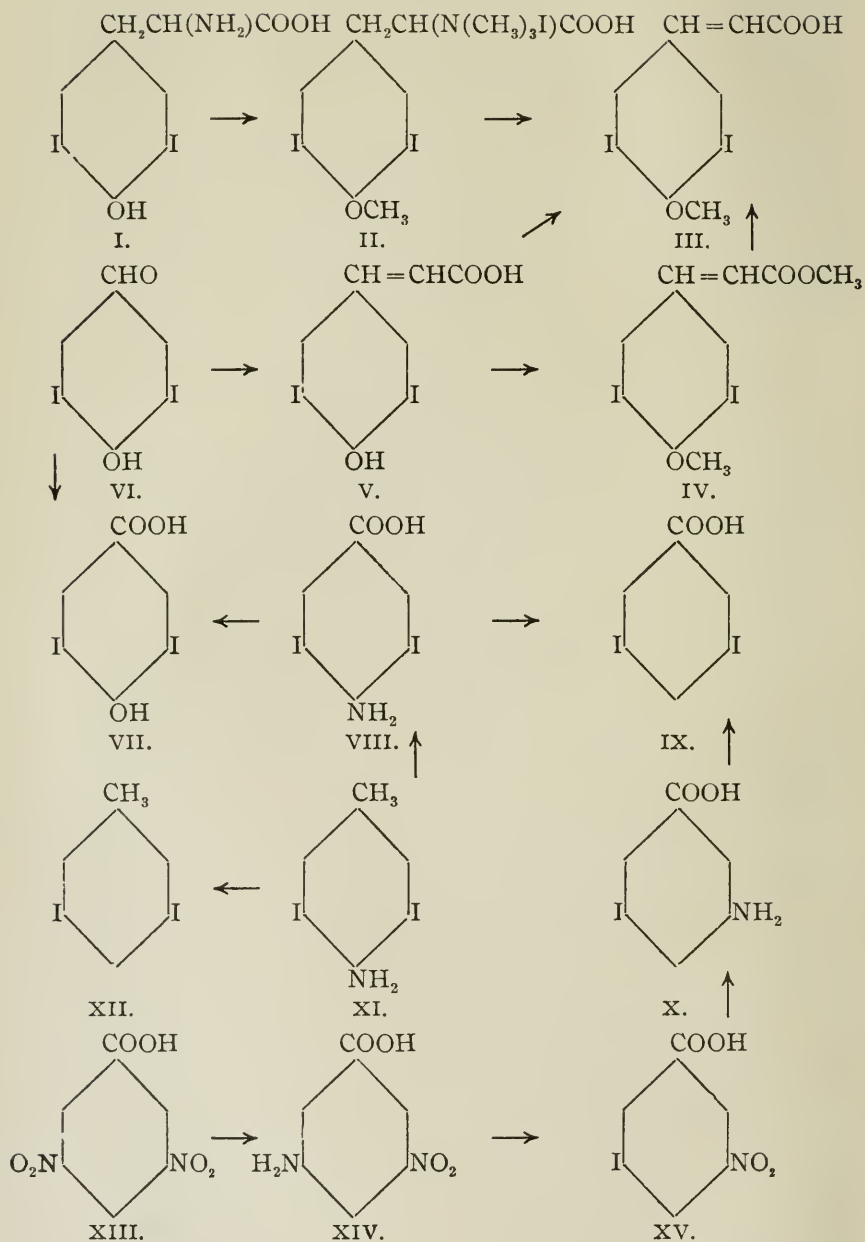
3,5-Diiod-p-*methoxycinnamic Acid from Diiodtyrosine.*—The tyrosine used was prepared from silk and casein by hydrolysis with dilute sulphuric acid in the usual manner. This was converted into diiodtyrosine in the manner described by Wheeler and Jamieson. It was purified by recrystallizing from water.

Two and seven-tenths grams of pulverized diiodtyrosine were suspended in about 80 cc. of methyl alcohol and 1.8 grams, or 5 molecular proportions, of potassium hydroxide were added. The acid quickly dissolved, forming a bright red solution. Eight grams of methyl iodide (the calculated amount for 5 molecules is 4.4 grams) were added and the solution was boiled for seven and a half hours in a flask attached to a return condenser. Crystalline material separated which was probably potassium iodide. The solution was evaporated to dryness and the residue was stirred and digested with cold water. The material left undissolved by this treatment then weighed 3.2 grams. This yield is more than the calculated for a simple methyl derivative. The calculated amount for a dimethylamino-*p*-methoxy methyl ester or a tetramethyl derivative is 3.04 grams. The calculated weight for a trimethyl ammonium iodide of the *p*-methoxy acid (II) is 3.84 grams.

This material dissolved easily in dilute alkali and readily in ethyl alcohol. It melted under the alcohol when warmed and it separated from a small volume of the solution in an amorphous condition. The whole was warmed with dilute sodium hydroxide. The solution had a strong odor of amine from the start and, after warming for 6 hours, concentrating, and cooling, shining scales or plates separated. Hydrochloric acid was added in slight excess. This produced an amorphous precipitate which weighed 2 grams. The calculated yield from a methoxytrimethylammonium iodide is 2.2 grams. This substance was practically insoluble in water and very soluble in methyl alcohol, and separated, on extreme concentration, in fine, small prisms. It was purified for analysis by dissolving in ethyl alcohol and precipitating with hot water. It separated in aggregates of minute prisms which melted at about 200° (Analysis I).

In another experiment, 5.4 grams of diiodtyrosine was methylated as above. The solution was boiled for 20 hours, the proportions used being 3.6 grams of potassium hydroxide, 100 cc. of methyl alcohol and 15 grams of methyl iodide. The product obtained was boiled with dilute sodium hydroxide, concentrated, and the crystalline sodium salt was filtered off, dissolved in water and the acid precipitated with hydrochloric acid. This preparation was used for comparison with that obtained by the following method:

*3,5-Diiod-*p-*methoxycinnamic Acid from 3,5-Diiod-*p-*hydroxy-benzaldehyde.*—Nine grams of *p*-hydroxybenzaldehyde gave, by Paal's method, 23.7 grams of diiod-*p*-hydroxybenzaldehyde melting at 198°, and 16.5 grams of this gave, by Perkins' synthesis, when carried out as described by Paal and Mohr, 11.1 grams of 3,5-diiod-*p*-hydroxycinnamic acid. The acid melted with decomposition at 247°. The above authors give 245°. Six grams of 3,5-diiod-*p*-hydroxycinnamic acid, 4.1 grams of potassium hydroxide in a few cc. of water, and 15 grams of methyl iodide were mixed in 100 cc. of methyl alcohol. The clear solution was allowed to stand overnight and was then warmed on the steam bath until it was no longer alkaline. The methyl alcohol was removed by evaporating to dryness and the residue was treated with water. A part dissolved and the insoluble portion was thoroughly washed with water. It weighed 2.8 grams and proved to be the methyl ester of 3,5-diiod-*p*-methoxycinnamic acid (see below).

On adding hydrochloric acid to the aqueous filtrate an amorphous white precipitate separated. This weighed 2.7 grams and when it was crystallized from 25–30 cc. of 95 per cent. alcohol it formed knobs or hard balls of minute prisms which melted quite sharply and completely at 198°–199°. An iodine determination agreed with the calculated value for 3,5-diiod-*p*-methoxycinnamic acid (Analysis II).

	Calculated for $C_{10}H_8O_3I_2$.	Found. I.	II.
I	59.07	59.21	58.96

This acid is practically insoluble in water, but readily soluble in methyl or ethyl alcohol. It separates from its solution

in alkalies on acidifying as a bulky, amorphous white precipitate, which becomes more compact on warming. It was found that chloroform was the best solvent to use for the purification of the substance. It is only moderately soluble in chloroform, from which it separates in the form of beautiful, long, silky needles. These melted constantly at 202°–203°. The acid melting at about 200°, obtained by Mr. Clapp from diiodtyrosine, was also crystallized from chloroform, whereupon the same long, silky needles melting at 202°–203° were obtained. When portions of the two samples were mixed the melting point was not altered.

The sodium salt and the methyl ester are the most characteristic derivatives of the acid.

The *Sodium Salt*, $CH_3OC_6H_2I_2CH = CHCOONa$. — Three grams of the acid were dissolved, by boiling, in 15 cc. of water containing 0.3 gram of sodium hydroxide; on cooling, a thick or bulky mass of very thin, pearly plates, or scales, was obtained. The mass was so thick that the test tube could be inverted without loss of the contents. The crystals were filtered off and recrystallized from water. They were very soluble in hot and only moderately soluble in cold water. They lost one per cent. of water at 110°, after drying over sulphuric acid for 2 days. A sodium determination gave:

	Calculated for $C_{10}H_7O_3I_2Na$.	Found.
Na	5.08	4.89

The *potassium salt* was found to be far more soluble than the sodium salt.

The *barium salt* formed a white, bulky precipitate when barium chloride was added to an aqueous solution of the sodium salt. It was difficultly soluble in boiling water and it crystallized in long, colorless needles.

The *silver salt*, prepared by adding silver nitrate to a solution of the sodium salt, was an amorphous white precipitate. It was insoluble in hot water and it did not darken when exposed to light for several days.

The *mercury salt*, from mercuric chloride and the potassium salt, formed a gelatinous precipitate insoluble in hot water.

The *copper salt* was obtained as an amorphous, light green precipitate on adding copper sulphate to a solution of the sodium salt. It was insoluble in hot water.

The *Methyl Ester of 3,5-Diiod*-p-*methoxycinnamic Acid*, $CH_3OC_6H_2I_2CH = CHCOOCH_3$.—As mentioned above, this ester was obtained, along with 3,5-diiod-*p*-methoxycinnamic acid, when 3,5-diiod-*p*-hydroxycinnamic acid was methylated with potassium hydroxide and methyl iodide. It is far less soluble in alcohol than the methoxy acid. While 2.7 grams of the acid dissolved in 25–30 cc. of alcohol, it required, on the other hand, about 200 cc. of hot 95 per cent. alcohol to dissolve 2.8 grams of the methyl ester. On cooling, very thin, elongated, shining, twinned plates were obtained. They were insoluble in water and melted to a clear, yellow oil at 173°–174°.

	Calculated for $C_{11}H_{10}O_3I_2$.	Found.
I	57.20	57.40

This same ester was obtained on esterifying the diiod-*p*-methoxycinnamic acid prepared from diiodtyrosine. Seven-tenths gram of the acid obtained by Mr. Clapp was dissolved in 25 cc. of methyl alcohol, 2 drops of concentrated sulphuric acid were added, and the solution was boiled for two hours. During the course of the reaction crystals separated and, on cooling, 0.5 gram of thin plates was obtained. These melted at 173°–174° and when mixed with the above sample the melting point was not altered. The two preparations were identical in every respect.

The *Ethyl Ester of 3,5-Diiod*-p-*methoxycinnamic Acid*, $CH_3OC_6H_2I_2CH = CHCOOC_2H_5$.—One gram of the acid was dissolved in 50 cc. of absolute alcohol containing 5 drops of concentrated sulphuric acid and the solution was boiled for 3 hours. As nothing separated the solution was evaporated to about 30 cc. whereupon, on cooling, 0.85 gram of crystals separated. They were recrystallized from alcohol and thus obtained in small, stout, colorless prisms which grew in fern-like clusters. This ester melted to a clear oil at 135° and was easily soluble in chloroform, difficultly soluble in alcohol, and insoluble in water. An iodine determination gave a re-

sult agreeing with the calculated value for ethyl 3,5-diiod-*p*-methoxycinnamate.

	Calculated for $C_{12}H_{12}O_3I_2$.	Found.
I	55.46	55.43

New Haven, Conn.,
June, 1909.

CLXXVII.—RESEARCHES ON PYRIMIDINES: THE THIO DERIVATIVES OF THYMINE AND THE PREPARATION OF THYMINE.[1]

[FORTY-NINTH PAPER.]

By Henry L. Wheeler and David F. McFarland.

In preparing uracil from ethylpseudothiourea hydrobromide and the sodium salt of ethyl formylacetate,[2] for some unknown reason it has sometimes happened that the yield obtained was very poor. A more satisfactory result was invariably obtained when sodiumformylacetate and thiourea were used.[3] The employment of thiourea instead of the pseudothiourea had the additional advantage of being a more direct process. It rendered unnecessary the preparation of the pseudothiourea and was therefore less expensive, and, perhaps better than all, the presence of mercaptan was avoided.

These results suggested that the preparation of thymine might be improved in a similar manner. When the sodium salt of ethyl formylpropionate was condensed with thiourea in aqueous solution (four experiments) we were surprised to find that the yield of 2-thiothymine (I) was invariably about one-half what would be expected from the pseudothiourea condensation under similar conditions. Obviously this was no improvement over our original method.

We have recently found, in other cases, that certain β-ketone esters condense with thiourea in alcoholic solution when they

[1] Part of a thesis presented by David F. McFarland for the degree of Ph.D., Yale, 1909.
[2] Wheeler and Merriam: This Journal, **29**, 478 (1903).
[3] Wheeler and Liddle: *Ibid.*, **40**, 547 (1908).

failed to do so in water. The condensation of ethyl sodium-
formylpropionate with thiourea was therefore carried out in
alcoholic solution (eight experiments). This brought about
the desired improvement. The yields were over twice those
obtained in the aqueous condensation.

For comparison with our original method ethyl sodium-
formylpropionate was condensed with ethylpseudothiourea
in aqueous (four experiments) and alcoholic (one experiment)
solutions.   It was then found that the average yield of 2-ethyl-
mercapto-5-methyl-6-oxypyrimidine,   in   these   experiments,
when expressed in the equivalent weight of thymine, was
nearly identical (20.9 per cent. of the calculated) with that
calculated from the average yield of 2-thiothymine obtained
in the alcoholic condensations (22.6 per cent. of the calcula-
ted).

In other words, almost the same amount of thymine is ob-
tained in these condensations whether we use thiourea in alco-
hol or pseudothiourea in water or alcohol. The use of thio-
urea, however, gives a little better yield and it is also to be
recommended for the reasons stated above. The condensa-
tion takes place as follows:

$$
\begin{array}{ccccc}
\mathrm{HNH} & \mathrm{C_2H_5OCO} & \mathrm{HN{-\!\!-}CO} & \mathrm{C_2H_5OH} \\
| & | & |\qquad| & \\
\mathrm{SC} \;+ & \mathrm{CCH_3} = & \mathrm{SC}\quad\mathrm{CCH_3}\;+ & \\
| & \| & |\qquad\| & \\
\mathrm{HNH} & \mathrm{NaOCH} & \mathrm{HN{-\!\!-}CH} & \mathrm{NaOH} \\
& & \mathrm{I.} &
\end{array}
$$
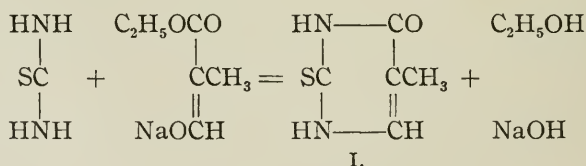
It is peculiar that a similar condensation failed to take place
in the case of urea and ethyl sodiumformylpropionate or
ethyl sodiumformylacetate[1] in either absolute alcohol or aqueous
solutions.

2-Thiothymine (I), like 2-thiouracil, is desulphurized and
quantitatively converted into thymine (V) by simply dis-
solving in water and evaporating to dryness with a slight ex-
cess of chloracetic acid.   The thymine prepared in this manner

[1] Wheeler and Liddle: *Loc. cit.*

melts higher and appears to be more readily purified than when prepared by means of a pseudothiourea.

We have prepared 6-thiothymine (II) and 2,6-dithiothymine (IV) in a manner similar to that used in the case of the corresponding uracil[1] and 4-methyluracil derivatives.[2] The preparation of the 6-thio derivatives in the thymine series is far less satisfactory than in the case of those previously described. The 2-ethylmercapto-5-methyl-6-thiopyrimidine (III), on boiling with hydrochloric acid, evolves mercaptan less easily than in the previous cases and the sulphur in the 6-position is also more or less removed at the same time, so that the yield is poor, or nothing but thymine is obtained. A similar behavior was observed in the preparation of 6-thiouracil but only on long warming with acid. On the other hand, 6-thio-4-methyluracil evolved mercaptan smoothly without being desulphurized in the 6-position.

2,6-Dithiothymine (IV) was prepared from 2-ethylmercapto-5-methyl-6-thiopyrimidine (III) by heating with dry hydrogen chloride.

We have found that the methylation of 6-thiothymine first gives 2-oxy-5-methyl-6-methylmercaptopyrimidine (VI), as would be expected, and on further methylation this compound yields the 3-methyl derivative, 2-oxy-3,5-dimethyl-6-methylmercaptopyrimidine (VII). This result is in accordance with the general tendency, previously observed by us, of a 6-mercapto-2-oxypyrimidine to alkylate in the 3-position.

2-Oxy-3,5-dimethyl-6-methylmercaptopyrimidine (VII), on boiling with hydrochloric acid, gives a quantitative yield of 3-methylthymine (VIII). These compounds and their transformations may be represented as follows:

[1] Wheeler and Liddle: *Loc. cit.*
[2] Wheeler and McFarland: THIS JOURNAL, **42,** 431 (1909).

```
HN——CS              HN——CS              HN——CS
 |     |              |     |              |     |
OC    CCH₃  ←  C₂H₅SC    CCH₃  →   SC     CCH₃
 |     ||             ||    ||            |      ||
HN——CH              N——CH              HN——CH
    II.                 III.                IV.
```

```
HN——CO              N═══CSCH₃           N═══CSCH₃
 |     |              |     |              |     |
OC    CCH₃  ←       OC     CCH₃  →   OC    CCH₃
 |     ||             |      ||            |      ||
HN——CH              HN——CH            CH₃N——CH
    V.                  VI.                VII.
```

```
HN——CO
 |     |
OC    CCH₃
 |     ||
CH₃N——CH
   VIII.
```
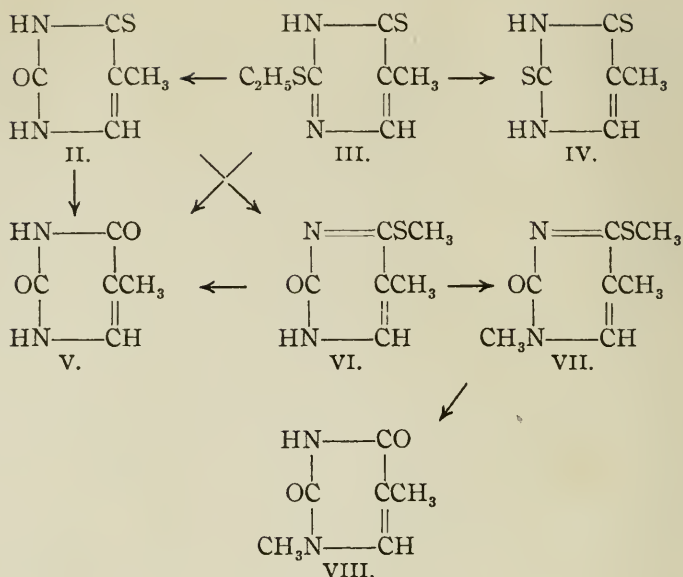
EXPERIMENTAL PART.

Ethyl Sodiumformylpropionate, $NaOCH = C(CH_3)CO_2C_2H_5$.— This salt was prepared, as Wislicenus directs,[1] in a manner similar to that used in the case of ethyl sodiumformylacetate. We have obtained the best results in the preparation of these salts when one atomic proportion of sodium was covered with dry ether in a flask attached to a return condenser and the mixture of esters slowly added. An excess of ethyl formate was employed and the amount of ether was sufficient to prevent the mixture from becoming thick. Three or four times the volume of the mixed esters was usually sufficient. If evaporation of the ether took place, owing to the esters being added too rapidly, or if not enough was present, the product frequently was sticky and difficult or impossible to filter. It therefore could not be washed with ether and dried satisfactorily. When 100 to 150 grams of each ester were used about a day and a half or two days was taken to add the mixture to the sodium. The sodium disappeared and the reaction was complete in about four days altogether.

In one experiment from 150 grams of ethyl propionate and

Ber. d. chem. Ges., **20**, 2934 (1887).

900 cc. of ether with one atomic proportion of sodium and 150 grams of ethyl formate, 145 grams of dry sodium salt were obtained. In the ether filtrate 9.6 grams of 2-thiothymine were found, or an equivalent of 32.3 grams more of sodium salt (see experiment XIV below). The total yield of crude sodium salt was therefore 177.3 grams for 150 grams of ethyl propionate, or 118.2 grams for 100 grams of ester.

In another experiment which was carried out in the same manner as the above, 50 grams of ethyl propionate gave 43.2 grams of dry sodium salt and an amount of 2-thiothymine (4.3 grams) in the ether filtrate (experiment XV) equivalent to 16.8 grams more of salt, making a total of 60 grams or 120 grams for 100 grams of ethyl propionate. This is 79 per cent. of the calculated. (See also experiment XIII below.) In the condensations in which we have used this crude salt, the yields of pyrimidine derivatives have in no case amounted to much over 30 per cent. of the calculated. The salt is obviously not pure, but whether or not this fact alone accounts for the low yield, or whether stereochemically different salts exist here, one form condensing and the other not, will have to be determined later.

Preparation of 2-Ethylmercapto-5-methyl-6-oxypyrimidine,[1]

$$\begin{array}{ccc} \text{HN} & \!\!\!\!\!\!\text{—} & \!\!\text{CO} \\ | & & | \\ \text{C}_2\text{H}_5\text{SC} & & \text{CCH}_3 \\ \| & & \| \\ \text{N} & \!\!\!\!\!\!\text{—} & \!\!\text{CH} \end{array}$$
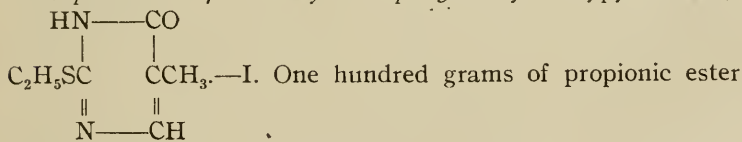
—I. One hundred grams of propionic ester and 80 grams of formic ester were added to 22.5 grams of sodium covered with ether. The ethyl sodiumformylpropionate was not filtered off but was condensed with 100 grams of pseudoethylthiourea hydrobromide by means of 65 grams of potassium hydroxide in about 750 cc. of water. On acidifying with acetic acid, after warming the mixture, 33 grams of 2-ethylmercapto-5-methyl-6-oxypyrimidine melting at 150° were obtained.

II. In another experiment 150 grams of propionic ester, 120 grams of formic ester and 33.7 grams of sodium were used. The product was mixed with a solution of 150 grams of ethylpseudothiourea hydrobromide and 97 grams of potas-

[1] See Wheeler and Johnson: THIS JOURNAL, **31**, 595 (1904).

suim hydroxide in about a liter of water. The yield of mer-captopyrimidine was 57.5 grams.

III. This experiment was carried out by Dr. Victor C. Myers. One hundred and fifteen grams of propionic ester, 100 grams formic ester and 26 grams of sodium in 250 cc. of ether were taken. The sodium salt was not filtered off but was condensed with 97 grams of ethylpseudothiourea hydro-bromide and 30 grams of potassium hydroxide. The solution was allowed to stand for 24 hours and then concentrated to one-half volume (300 cc.?) before precipitating with dilute acetic acid. The precipitate weighed 61.5 grams. This probably contained some potassium and sodium salts since on recrystallizing from water 40 grams of material melting at 158°–159° was obtained.

IV. The above experiment was repeated with the same quantities and under the same conditions. The first portion of mercapto compounds separated weighed 53.3 grams. When recrystallized from water 38.3 grams of pure material were obtained. The mother liquor contained sodium and potassium salts.

V. In this experiment the condensation was tried in alcohol. Thirteen and a half grams of dry ethyl sodiumformyl-propionate were mixed with 16.4 grams of ethylpseudothiourea hydrobromide in 300 cc. of absolute alcohol in which 2.0 grams of sodium had been dissolved. Complete solution did not take place. The mixture was shaken and let stand for 20 hours, then warmed on the steam bath, evaporated to dryness and dissolved in 60 cc. of water and precipitated with acetic acid. The precipitate weighed 3.85 grams.

The following table gives a further comparison of the above results:

	Weight of ethyl propionate.	Weight of ethyl so-diumformyl-propionate.	Weight of mercapto derivative obtained.	Calculated weight of mercapto derivative per 100 grams ester.	Per cent. yield of mercapto derivative.	Calculated weight of thymine from 100 grams ester.
I	100	120[1]	33.0	33.0	19.75	24.4
II	150	180[1]	57.5	38.3	22.9	28.4
III	115	138[1] -	61.5	53.3	31.9	39.5
IV	115	138[1]	53.2	46.3	27.7	34.3
V	...	13.5	3.85	33.7	20.2	24.9

[1] Calculated from average yield of salt.

If we exclude experiments III and IV, in which the results are a little too high, as already stated, the average yield of thymine is 25.9 grams from 100 grams of ethyl propionate (or including these results it is 30.3 grams). Twenty-five and nine-tenths grams of thymine is 20.9 per cent. of the theoretical amount calculated directly from the ethyl propionate.

Preparation of 2-Thiothymine,
$$\begin{array}{ccc} \text{HN} & \!\!\!\!\text{---}\!\!\!\! & \text{CO} \\ | & & | \\ \text{SC} & & \text{CCH}_3, \\ | & & \| \\ \text{HN} & \!\!\!\!\text{---}\!\!\!\! & \text{CH} \end{array}$$
in Alcoholic
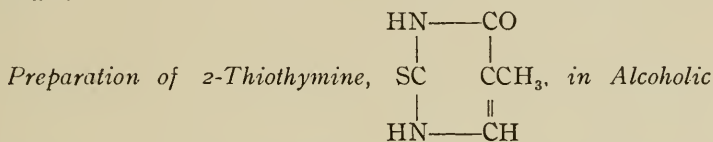
Solution.—VI. Nineteen grams of ethyl sodiumformylpropionate, pressed on paper and dried until all odor of ether had disappeared, were added to a solution of 9.5 grams (one molecule) of thiourea and 2.9 grams of sodium in 350 cc. of absolute alcohol. The mixture was warmed for 3 hours, evaporated to dryness, dissolved in 80 cc. of water and precipitated with dilute acetic acid. The crystalline precipitate weighed 6.8 grams.

VII. Twenty-eight grams of the sodium salt were warmed for five hours with 14 grams (1 molecule) of thiourea in 400 cc. of absolute alcohol, then evaporated to dryness, dissolved in water and precipitated with acetic acid. The yield in this case was 8.0 grams.

VIII. Fourteen and one-tenth grams of the dry sodium salt were treated with the same relative proportions of the thiourea, sodium ethylate, and alcohol and under the same conditions as in experiment VI. The yield of 2-thiothymine was 3.4 grams.

IX. Fifteen grams of the sodium salt, 4 grams of thiourea (about one-half molecule) and 2.2 grams of sodium dissolved in 150 cc. of absolute alcohol were mixed and heated for 3 hours. Then 25 cc. of water were added and the whole evaporated to dryness. The residue was taken up in 60 cc. of water and precipitated with acetic acid. The precipitate weighed 4.0 grams. On recrystallizing from 17.5 cc. of alcohol 3.4 grams separated.

X. Twenty-seven grams of the sodium salt were warmed with 13.5 grams (one molecule) of thiourea and 4.3 grams of sodium in 350 cc. of 95 per cent. alcohol for three and a half hours. There remained considerable material undissolved. The alcohol was evaporated and the residue was dissolved in 140 cc. of water. The addition of acetic acid to this solution gave 8.0 grams of 2-thiothymine.

XI. Thirteen and two-tenths grams of sodium salt were warmed with 3.5 grams of thiourea (a little over one-half molecule) and 2 grams of sodium in 150 cc. of 95 per cent. alcohol for 3 hours. Twenty-five cc. of water were added and the solution was warmed for a half hour, then evaporated to dryness. The residue was taken up in 60 cc. of water and precipitated, whereupon 3.3 grams of 2-thiothymine were obtained.

XII. Fifteen grams of dry sodium salt were warmed 3 hours with 4 grams of thiourea (one-half molecule + 0.5 gram) and 2.3 grams of sodium dissolved in 100 cc. of 85 per cent. alcohol. The sodium salt was first dissolved in 15 cc. of water and then the sodium ethylate and thiourea were added. Some solid separated after warming, 10 cc. more water were added and the solution heated for a half hour longer. On evaporating to dryness, dissolving in 60 cc. of water and precipitating, 3.8 grams of 2-thiothymine were obtained. On recrystallizing from 175 cc. of water 3.2 grams separated.

XIII. Fifty grams of ethyl propionate, 43.5 grams of ethyl formate and 11.3 grams of sodium gave 47.5 grams of dry ethyl sodiumformylpropionate. The ether filtrate was evaporated to dryness and the residue was combined with the above. Calculating on the basis of 65 grams of sodium salt in the entire lot, twenty grams of thiourea (over half molecule) in 500 cc. of 95 per cent. alcohol were added. The mixture was heated three and a half hours, the alcohol was then evaporated and the residue dissolved in 175 cc. of water. When precipitated as in the previous cases, 15 grams of 2-thiothymine were obtained.

XIV. The ether filtrate from a condensation in which 150 grams of ethyl propionate were converted into sodium salt

was evaporated to dryness and treated with 4 grams of sodium in 400 cc. of absolute alcohol and 20 grams of thiourea. The mixture was heated one hour on the steam bath and then evaporated to dryness. Two hundred and fifty cc. of water were added and the solution, on precipitating with acetic acid, gave 9.6 grams of 2-thiothymine. From the average yield of four condensations with the filtered salt it is calculated that the ether solution in this case contained 32.3 grams of ethyl sodiumformylpropionate.

XV. The ether filtrate from the preparation of ethyl sodiumformylpropionate in which 50 grams of ethyl propionate were used was treated as above with 3 grams of sodium in 100 cc. of absolute alcohol and 5 grams of thiourea. The mixture was warmed for 3 hours, then 35 cc. of water were added and the solution was warmed for a half hour longer. On evaporating to dryness, taking up in 50 cc. of water, and adding acetic acid 4.3 grams of 2-thiothymine were obtained.

The following table gives the results of the condensation of ethyl sodiumformylpropionate with thiourea in alcoholic solutions:

	Weight of ethyl sodiumformyl-propionate.	Number of cc. of alcohol for 1 gram of sodium salt.	Weight of 2-thio-thymine obtained.	Calculated weight of 2-thio-thymine from 100 grams ester.	Per cent. yield of 2-thio-thymine.	Calculated weight of thymine from 100 grams ester.
VI	19.0	18.4	6.8	42.3	30.4	37.6
VII	28.0	14.3	8.0	33.8	24.2	30.0
VIII	14.1	18.4	3.4	28.6	20.5	25.3
IX	15.0	10.0	4.0	32.0	23.0	28.4
X	27.0	13.0	8.0	35.0	25.1	31.0
XI	13.2	11.3	3.3	30.0	21.6	26.6
XII	15.0	5.7	3.8	30.4	21.8	27.0
XIII	60.0?	8.3	15.0	30.0	20.1	24.8

Experiments VI, VII, VIII and IX were carried out in absolute alcohol, X, XI and XIII in 95 per cent. alcohol, and XII in 85 per cent. alcohol. Experiment VIII is a duplicate of VI. Sodium ethylate and the calculated quantity of thiourea were present. Number VII was similar except that no sodium ethylate was used. In IX sodium ethylate was present but only one-half the calculated quantity of thiourea

was added. In the remaining experiments sodium ethylate and about one-half the calculated quantity of thiourea was employed, except in X, where one molecular proportion of thiourea was used.

If we exclude experiment VI, which for some unknown reason gave a much higher yield of 2-thiothymine than the others, and also experiment XIII, in which the amount of salt taken was determined by calculation, we find that the average yield of thymine by this method is 28.0 grams from 100 grams of ethyl propionate. This is 22.6 per cent. of the calculated.

Preparation of 2-Thiothymine in Aqueous Solution.—XVI. Seventeen grams of ethyl sodiumformylpropionate were dissolved in a solution of 8.5 grams (one molecule) of thiourea in 65 cc. of water. The solution was allowed to stand for 10 hours, then precipitated with acetic acid. The yield of 2-thiothymine was 2.5 grams.

XVII. (By WALTER F. STOREY.) One hundred grams of propionic ester were condensed with an excess of ethyl formate and a little over (2 grams) one atomic proportion of sodium. When all the sodium had disappeared the calculated quantity (one molecule) of thiourea was added in ice water and the mixture thoroughly shaken. After standing overnight the ether was removed and, after warming, concentrating and cooling, acetic acid was added. The yield was 14.5 grams of the thiopyrimidine.

XVIII. One hundred and fifty grams of ethyl propionate, 115 grams of ethyl formate and 36 grams instead of 33.8 of sodium were used in this experiment. When the sodium had disappeared a solution of 55 grams of thiourea in 400 cc. of water was prepared (38 grams is one-half the calculated amount). Lumps of ice were added to the solution of the salt and the ether solution. The whole was shaken and allowed to stand overnight. The deep red solution was concentrated on the steam bath and finally cooled and acetic acid added. The precipitate weighed 27 grams, and from the filtrate 3 grams more were obtained on standing.

XIX. One hundred grams of each ester were condensed with 2 grams more than the calculated amount of sodium.

The whole was mixed with a saturated solution of 70 grams of thiourea in ice water. After standing a few minutes it was warmed and acetic acid added. Fifteen grams of 2-thiothymine were obtained.

The following table gives the results of the condensation of ethyl sodiumformylpropionate with thiourea in aqueous solution.

	Weight of propionic ester.	Weight of ethyl sodium-formyl-propionate.	Weight of 2-thio-thymine obtained.	Calculated weight of 2-thio-thymine from 100 grams ester.	Per cent. yield of 2-thio-thymine.	Calculated weight of thymine from 100 grams ester.
XVI	...	17^1	2.5	17.4	12.5	15.4
XVII	100	120^1	14.5	14.5	10.4	12.8
XVIII	150	180^1	30.0	20.0	14.4	17.7
XIX	100	120^1	15.0	15.0	10.7	13.3

The average yield of thymine by this method is 14.8 grams from 100 grams of ethyl propionate. This is only 11.9 per cent. of the calculated.

$$\begin{array}{ccc} \text{HN} & \!\!\!-\!\!\!- & \text{CO} \\ | & & | \\ \text{OC} & & \text{CCH}_3 \\ | & & \| \\ \text{HN} & \!\!\!-\!\!\!- & \text{CH} \end{array}$$
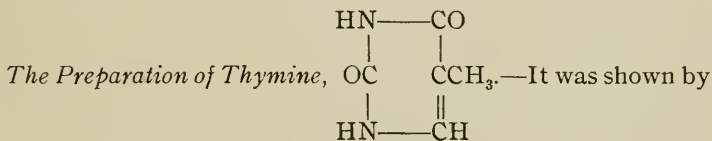
The Preparation of Thymine, ——It was shown by Wheeler and Merriam that 2-methylmercapto-5-methyl-6-oxypyrimidine[2] gave 99 per cent. of the calculated amount of thymine when boiled with hydrochloric acid. The ethyl-mercapto derivative gives a similar result.

2-Thiothymine, like 2-thiouracil, is easily desulphurized by simply evaporating its aqueous solution with chloracetic acid.[3] For example, 3 grams of 2-thiothymine were dissolved in 250 cc. of boiling water and 3 grams of chloracetic acid were added. The solution was then evaporated to dryness on the steam bath and the residue was washed with 15–20 cc. of alcohol. It was free from sulphur and weighed 2.55 grams or 95.8 per cent. of the calculated. On evaporating the alcoholic washings more was obtained. The washed ma-

[1] Calculated from average yield of salt.
[2] THIS JOURNAL, **29,** 487 (1903).
[3] *Ibid.,* **40,** 552 (1908).

terial consisted of snow-white crystals or scales and it melted at 340°. This is a higher melting point than that observed for thymine from other sources. Fischer and Roeder[1] give 321°, Wheeler and Merriam[2] 326°. A nitrogen determination by W. F. Storey gave:

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.21

In desulphurizing larger quantities it is unnecessary to dissolve all the material at first and relatively less chloracetic acid may be used.

Properties of 2-Thiothymine.—The properties of 2-thiothymine and its salts have been investigated by W. F. Storey. When the substance is first obtained by acidifying the alkaline solutions with acetic acid it separates slowly, usually not all at once, as a crystalline brownish-white precipitate. It has about the same solubility in water as in alcohol and it crystallizes from these solvents in fairly stout prisms, which have a tendency to retain the color of the solutions. One hundred parts of water at 20° dissolved 0.133 part of 2-thiothymine. This is the average of two closely agreeing determinations. Thymine is more than twice as soluble in water. Mr. Storey found that 100 parts of water at 23° dissolved 0.303 part thymine.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.71	19.67

2-Thiothymine has more pronounced acid properties than thymine. When crystallized from aqueous ammonia it retains ammonia. On drying, the amount of ammonia retained (21.86 per cent. nitrogen) was less than that calculated for a 1 : 1 salt (26.41 per cent. nitrogen). The salts of the alkali metals are very soluble in water. A solution of the sodium salt gave with silver nitrate an amorphous white precipitate, which did not blacken on boiling. The boiling

[1] Ber. d. chem. Ges., **34**, 3751 (1901).
[2] *Loc. cit.*

aqueous solution gives a white precipitate with mercuric chloride. It did not blacken on boiling alone or in the presence of alkali.

The sodium salt of 2-thiothymine, $C_5H_5ON_2SNa.1.5H_2O$, appears to be less soluble than the potassium salt. It was formed by dissolving the pyrimidine in water containing the calculated quantity of sodium hydroxide, concentrating and then crystallizing from aqueous alcohol. It formed radiating prisms which did not melt at 300°.

	Calculated for $C_5H_5ON_2SNa.1.5H_2O$.	Found.	
N	14.73	14.73	14.58
H_2O	14.21	14.65	...

The potassium salt, $C_5H_5ON_2SK.H_2O$, is soluble in less than three parts of water. From dilute alcohol it forms radiating, colorless prisms, similar to the sodium salt.

	Calculated for $C_5H_5ON_2SK.H_2O$.	Found.
N	14.14	13.83

The Copper Salt, $C_5H_4ON_2SCu.H_2O$.—This salt was prepared by adding copper sulphate in aqueous solution to a hot saturated aqueous solution of 2-thiothymine. It formed a green, amorphous precipitate, which was washed with water and dried over sulphuric acid.

	Calculated for $C_5H_4ON_2SCu.H_2O$.	Found.
N	12.58	12.52
H_2O	8.08	7.79

It may be mentioned that the corresponding copper salt of 2-thiouracil, which also contains one molecule of water,[1] has a mustard-yellow color. These salts do not blacken on boiling. List[2] found that 2-thio-4-methyluracil in hot, saturated, aqueous solution gave a yellow precipitate with copper sulphate (this salt was anhydrous), while if the potassium salt was used a green copper salt was obtained.

[1] Wheeler and Liddle: *Loc. cit.*
[2] Ann. Chem. (Liebig), **236**, 9, 11 (1886).

2-Benzylmercapto-5-methyl-6-oxypyrimidine,

$$HN\!-\!-\!CO$$

$C_6H_5CH_2SC \quad CCH_3$ (By W. F. STOREY).—This was prepared

$$N\!-\!-\!CH$$
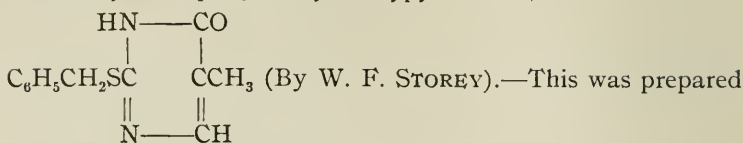
from the above potassium salt by warming in alcoholic solution with benzyl chloride. From dilute alcohol it formed colorless needles, which melted to a clear oil at 204°–205°.

	Calculated for $C_{12}H_{12}ON_2S$.	Found.
N	12.07	12.25

2-Ethylmercapto-5-methyl-6-thiopyrimidine,

$$HN\!-\!-\!CS$$

$C_2H_5SC \quad CCH_3$.—An alcoholic solution of potassium hydro-

$$N\!-\!-\!CH$$
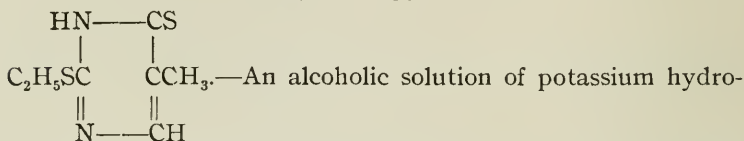
sulphide was prepared by saturating a solution of 57 grams of potassium hydroxide in 250 cc. of alcohol with hydrogen sulphide. To this solution 24 grams of 2-ethylmercapto-5-methyl-6-chlorpyrimidine[1] were added. The reaction began immediately and after warming on the steam bath for nearly an hour the solution was evaporated to dryness. The residue dissolved completely in water and on acidifying with acetic acid a bulky precipitate separated. After washing with water and drying it was found that the yield was practically quantitative. The crude material melted at about 175° to a clear oil and on further heating it solidified at 180°–190° and remained solid until 280° was reached, when it melted with some effervescence. The substance dissolved easily in boiling alcohol. When the solution was quickly cooled the material crystallized in plates, but when allowed to cool slowly, prismatic needles separated. It then melted at 181° to a clear oil; the pure material, on further heating, did not solidify.

	Calculated for $C_7H_{10}N_2S_2$.	Found.
N	15.05	14.91

[1] Wheeler and Johnson: THIS JOURNAL, **31**, 595 (1904).

```
           HN——CS
            |    |
2,6-Dithiothymine,  SC    CCH₃.
            |    ||
           HN——CH
```
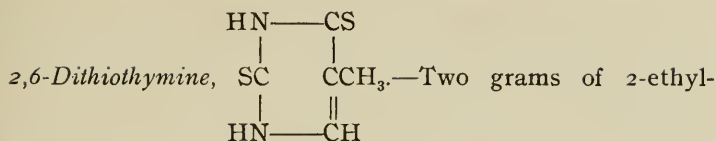
2,6-Dithiothymine, SC CCH$_3$.—Two grams of 2-ethyl-mercapto-5-methyl-6-thiopyrimidine were heated in an oil bath at 215°. The substance melted and a small portion sublimed. On passing perfectly dry hydrogen chloride into the molten mass the material almost immediately solidified. The passage of the gas was continued for about five minutes. After cooling, the solid was treated with ammonium hydroxide, which dissolved the greater part, leaving a small amount of a pungent smelling oil. This was separated from the ammonia solution and the latter was acidified with acetic acid. A bulky yellow precipitate resulted, which was only slightly soluble in water but dissolved fairly easily in alcohol, and then, on cooling, gave bunches of small, bright yellow needles. They melted at 281° with decomposition and effervescence.

	Calculated for C$_5$H$_6$N$_2$S$_2$.	Found.
N	17.94	18.14

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           HN——CS
            |    |
6-Thiothymine,  OC    CCH₃.
            |    ||
           HN——CH
```
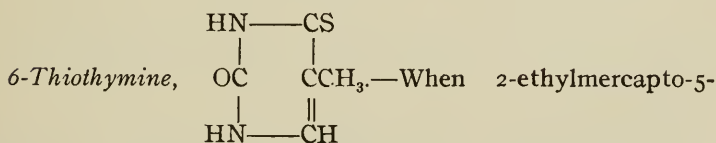
6-Thiothymine, OC CCH$_3$.—When 2-ethylmercapto-5-methyl-6-thiopyrimidine is heated with strong hydrochloric acid it does not smoothly go into 6-thiothymine as might be expected from analogy with the corresponding 4-methyl compound, but instead it shows a strong tendency to lose sulphur from the 6-position and pass directly into thymine. In fact, by boiling ten grams of the 2-ethylmercapto-6-thiopyrimidine for one and a half hours with strong hydrochloric acid and then twice evaporating to dryness with additional acid, very pure thymine was obtained which, after one recrystallization, gave no test for sulphur and melted at 340°. A nitrogen determination gave 22.22 per cent. nitrogen. This is the calculated value for thymine.

By a less vigorous treatment with acid, the decomposition

was not carried so far and a small yield of 6-thiothymine was obtained. Several experiments were required to show the conditions best adapted to obtaining this result. It was found advisable to stop the hydrolysis while there still remained some unchanged mercapto derivative. This was then extracted by means of alcohol, leaving a mixture of 6-thiothymine with a small amount of thymine. These were separated by crystallizing from water.

Nine grams of 2-ethylmercapto-5-methyl-6-thiopyrimidine were twice evaporated to dryness on the steam bath with 45 cc. of concentrated hydrochloric acid and an equal quantity of water. The dry residue was boiled for a few minutes with 100 cc. of alcohol and the portion which remained undissolved was filtered off. This weighed 4.2 grams. It was dissolved in boiling water and on cooling gave bright yellow, matted, silky needles, which melted with some effervescence at 330°.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.72	19.98

2-Oxy-5-methyl-6-methylmercaptopyrimidine,

$$\begin{array}{l} N\!\!=\!\!=\!\!CSCH_3 \\ |\qquad | \\ OC\qquad CCH_3.\text{—Four grams of 6-thiothymine were dissolved} \\ |\qquad \| \\ HN\!\!-\!\!-\!\!CH \end{array}$$

with 1.58 grams of potassium hydroxide in 125 cc. of alcohol and 20 cc. of water. The change from the yellow pyrimidine to the potassium salt was marked by an immediate change to a white color. Four grams of methyl iodide were added to the solution and the mixture was warmed for 15 minutes on the water bath and then allowed to stand overnight. The reaction was complete at the end of this time and the solution became neutral. The alcohol was evaporated and the residue was found to be easily soluble in hot water. On crystallizing from this solvent bunches of light yellow, prismatic needles were obtained which, after two recrystallizations from alcohol, melted at 205°–211°.

	Calculated for $C_6H_8ON_2S$.	Found. I.	II.
N	17.94	18.08	18.14

2-Oxy-3,5-dimethyl-6-methylmercaptopyrimidine,

$$\begin{array}{cc} N=\!=\!CSCH_3 \\ | \quad\quad | \\ OC \quad\quad CCH_3 \\ | \quad\quad \| \\ CH_3N\!-\!-\!-\!CH \end{array}$$
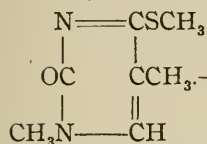
—Four and seven-tenths grams of potassium hydroxide and 4.4 grams of 2-oxy-5-methyl-6-methylmercaptopyrimidine were dissolved in 150 cc. of 95 per cent. alcohol. Twelve grams of methyl iodide, or three molecular quantities, were added and the mixture was warmed for an hour on the steam bath under a return condenser. The solution then became neutral. After evaporating off the alcohol, the solid residue was extracted three times with boiling chloroform. An oily residue separated from the chloroform solution which solidified to a white solid on being stirred. It weighed 4.5 grams, or 94 per cent. of the theoretical amount of dimethylmethylmercaptopyrimidine. This material was extremely soluble in alcohol. It also dissolved easily in boiling water and benzene. From benzene solutions it crystallized in clusters of crystals resembling grains of wheat. From the water solutions, which had a marked tendency to remain supersaturated even after standing several hours, the substance crystallized in white, prismatic needles, which melted to a colorless oil at 83°.

	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.4	16.6

Treatment with Hydrochloric Acid: 3-Methylthymine.—In order to determine the structure of the above compoud two grams of it were boiled for 3 hours with 25 cc. of concentrated hydrochloric acid and an equal quantity of water, under a return condenser. On evaporating off the acid 1.4 grams of a white solid was left behind, which melted at 281°–283°. One crystallization of this from water gave one gram of material melting at 284° and exhibiting all the properties of 3-methylthymine, as described by Johnson and Clapp.[1] Especially noticeable were the two forms of crystals (needles and prisms)

[1] J. Biol. Chem., **5**, 49 (1908).

described. When this sample was mixed with a sample of their material the melting point was unchanged.

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.0	20.1

The mother liquor from this compound was carefully examined for the isomeric 1-methylthymine, but this substance was not found.

In order to determine whether or not any of the isomeric 2-oxy-1,5-dimethyl-6-methylmercaptopyrimidine had been formed with the 3,5-dimethyl derivative, the mother liquors from the crystallization of 2-oxy-3,5-dimethyl-6-methyl-mercaptopyrimidine were boiled for 3 hours with hydrochloric acid, under a return condenser. After evaporating the acid the solid residue weighed 1.1 grams. From this, by crystallizing from water, were recovered 0.8 gram of nearly pure 3-methylthymine, melting at 275°–281° and showing the characteristic properties. There was also obtained a very small quantity (0.15 gram) of another substance which sublimed in white needles. This substance melted at 153°–155° and was extremely soluble in water and alcohol. Not enough was obtained for analysis, but it is probable that it was 1,3-dimethylthymine, described by Johnson and Clapp. They give the melting point as 153°. When our material was mixed with theirs the melting point was not lowered. The formation of 1,3-dimethylthymine may be explained by supposing a small amount of thymine to have been left in the 6-thiothymine. The difficulty of obtaining 6-thiothymine free from thymine has been noted above. Thymine, on methylation, would give 1,3-dimethylthymine.

No evidence could be found here of the presence of 1-methylthymine. It seems fair to conclude, therefore, that under the conditions employed in the methylation of this 6-methyl-mercaptopyrimidine only a 3-derivative was formed.

THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION, AND THE EFFECT OF TEMPERATURE ON SUCH SPECTRA.

[TWENTY-SIXTH COMMUNICATION.]

By Harry C. Jones and W. W. Strong.

(A report on part of the work on absorption spectra that is being carried on with the aid of a Grant from the Carnegie Institution of Washington.)

PART I.—THE ABSORPTION SPECTRA OF VARIOUS POTASSIUM, URANIUM AND NEODYMIUM COMPOUNDS.

Outline.—I. Experimental Methods and Preparation of Solutions. II. Absorption Spectra of Potassium Salts in Aqueous Solutions. III. The Absorption Spectra of Uranium Compounds. IV. The Absorption Spectrum of Uranyl Chloride: (*a*) in Water, (*b*) as Affected by Calcium and Aluminium Chlorides, (*c*) in Methyl Alcohol, (*d*) as an Anhydrous Salt, (*e*) in Methyl Alcohol and Water, (*f*) in Ethyl Alcohol, (*g*) with Calcium Chloride in Methyl Alcohol. V. The Absorption Spectrum of Uranyl Nitrate: (*a*) in Water, (*b*) as a Crystalline Salt, (*c*) as Affected by Dilution, (*d*) in Methyl Alcohol, (*e*) in Mixtures of Methyl Alcohol and Water, (*f*) in Ethyl Alcohol, (*g*) as an Anhydrous Salt. VI. The Absorption Spectra of Uranyl Bromide, Sulphate and Acetate: (*a*) Uranyl Bromide in Water, (*b*) Uranyl Sulphate in Water, (*c*) Uranyl Acetate in Water, (*d*) the Anhydrous Acetate, (*e*) Uranyl Acetate in Methyl Alcohol, (*f*) the Bands of the Acetate. VII. The Phosphorescence and Fluorescence of Uranium Compounds. VIII. The Absorption Spectrum of Uranous Salts. IX. The Various Uranium Spectra. X. The Absorption Spectra of Neodymium Salts: (*a*) in Glycerol. XI. Summary.

Description of Plates.

Plate I. Uranyl Chloride in Methyl Alcohol.—A. Beer's Law. B. Depth Cell Constant, 6 mm.

Plate II. Uranyl and Calcium Chlorides in Methyl Alcohol. Depth Cell Constant.—A. 6 mm. B. 3 mm.

Plate III. Uranyl Nitrate, Sulphate and Acetate.

Plate IV. A. Uranyl Nitrate. B. Uranous Chloride.

Plate V. Uranyl Bromide in Water.—A. Beer's Law. B. Depth Cell Constant.

Plate VI. Uranyl Acetate in Water.—A. Beer's Law. B. Depth Cell Constant.

Plate VII. A. Uranous Sulphate. B. Uranous Chloride.

Plate VIII. Uranous Chloride.—A. In Water. B. In Methyl Alcohol.

I. Experimental Methods.

On account of the large number of bands in the absorption spectra of uranium and the rare earth salts, a study of these spectra is more interesting and more fruitful of results than the study of the spectra of the ordinary colored salts like those of nickel or copper. The absorption spectra of the ferricyanide, ferrocyanide, chromate and dichromate of potassium, the acetate, bromide, chloride, nitrate and sulphate of uranyl in water, the acetate, nitrate and chloride of uranyl in methyl alcohol, and the nitrate and chloride of uranyl in ethyl alcohol have been mapped, and Beer's law, as well as the effect of foreign substances on the absorption spectra, have been tested for these salts. The absorption spectra of two uranous salts, the chloride and sulphate, have been photographed and those of neodymium chloride in pure glycerol and in mixtures of glycerol and water have been studied. In this work the methods used by Jones and Uhler[1] and Jones and Anderson[2] have in the main been employed.

The investigations of the effect of changes in temperature on the absorption spectra of solutions have been confined to different concentration of aqueous solutions of the chloride, nitrate, acetate, sulphate and sulphocyanate of cobalt, the chloride, acetate and sulphate of nickel, the chloride, sulphate and acetate of chromium, chrome alum, the nitrate and bromide of copper, uranous chloride, erbium chloride, the chloride and nitrate of praseodymium, the sulphate, acetate, chloride and nitrate of uranyl, and the chloride, bromide and nitrate of neodymium. Spectrograms of the absorption spectra for a given concentration of a salt, with a constant thickness of layer, have been made for every 15° between 0° and 90° C.

To make a spectrogram, light from a Nernst glower and from a spark is allowed to pass through the solution that is being investigated. It is then focused upon the slit of a spectroscope, and, falling then on a concave grating, is spread out into a spectrum on the film upon which it is photographed. The films used were made by Wratten and Wainwright, of

[1] Carnegie Institution of Washington, Publication No. 60.
[2] *Ibid.*, No. 110.

Croyden, England, and were very uniformly sensitive to light
from λ 2100 to λ 7200.

The sectional diagram (Fig. I) will make the experimental
arrangement of the apparatus clearer. N is a Nernst glower
which is arranged to slide along the rod AB. P and P' are
quartz prisms which are held by a lid L. The prism P is
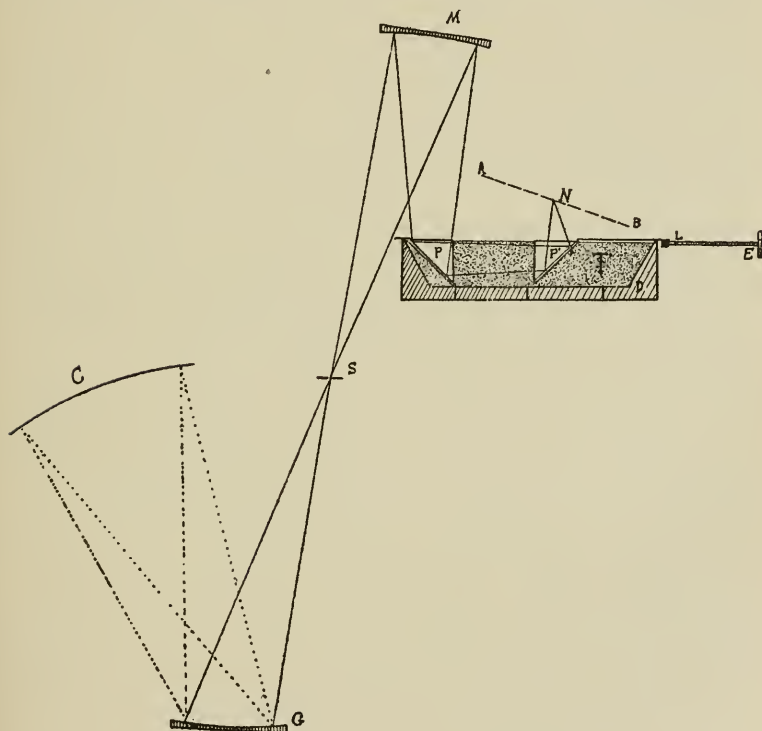
Fig. I.

stationary, whereas the prism P' can be moved by the travel-
ing carriage E back and forth through the trough T, which
contains the solution whose absorption spectrum is being in-
vestigated. AB is so inclined that the optical length of the
light beam from N to P', P and the concave mirror M shall
be constant, whatever the length of the solution between P
and P' may be. The greatest length of path PP' used was

200 mm. The hypothenuse faces of P and P' are backed by air films which are enclosed by glass plates cemented to the quartz prisms

Considerable difficulty was experienced in finding a cement that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work fairly well. D is a brass box holding the trough T. D is filled with oil and is placed in a water bath whose temperature can be varied between 0° and 90° C. The path of the beam of light is then from the Nernst glower (N) or spark to the quartz prism P'. The light is totally reflected from the hypothenuse face of this prism through the solution to P. This prism also has its hypothenuse face backed by an air-film, so that the light is totally reflected upwards to the concave speculum mirror at M. M focuses the light on the slit of the Rowland concave grating spectroscope, G being the grating and C the focal curve of the spectrum. The prism arrangement was designed by Dr. John A. Anderson.

This apparatus was found to work very well for aqueous solutions. Some evaporation took place at the higher temperatures, but distilled water was added in proper quantity and mixed with the solution so as to keep the concentration constant. By using troughs of different lengths it was possible to vary the length of salt solution through which the light beam passed from 1 to 200 mm. One inconvenience was experienced at low temperatures; moisture would sometimes condense upon the exposed prism faces. To overcome this an air blast was directed upon these faces and this helped very materially to prevent the condensation of moisture.

For the investigation of glycerol and other solutions a cell made of fused silica was used. The cell, as received from the Silica Syndicate Company, did not have plane parallel ends. At the suggestion of Dr. Pfund these were ground down with finely powdered emery and rouge. In this way a very serviceable cell was obtained.

For work on the effect of high temperatures on absorption spectra, a closed iron cell is being made. This is intended to stand the pressures exerted by the alcohols, acetone, ether,

water, etc., at their critical temperatures. The ends will contain quartz windows and the whole interior of the cell will be lined with gold. At the same time a radiomicrometer is being made and an apparatus is being devised by means of which quantitative measurements of the energy absorption for all parts of the spectrum can be obtained. A fuller description of the apparatus will be given later.

In the case of solids, the time of exposure is necessarily long, usually occupying several hours. It is very necessary in this case to screen off stray light. The method is very simple—consisting in focusing by means of mirrors or lenses the light from a Nernst glower or an arc upon the salt. The salt is placed a short distance from the slit of the spectroscope so that the directly reflected light does not enter the slit. By this means only the diffusely reflected light enters the slit and in general this light has penetrated somewhat into the salt and, accordingly, some wave lengths are partly or wholly absorbed. The salt is placed at such a distance that the grating is completely filled with the beam of diffusely reflected light entering the slit. This method has been used by several investigators, notably by Anderson[1] and Schultz.[2]

The observations on the phosphorescence of uranium compounds were made with the Hilger spectroscope, from which wave lengths can be read directly. Either sunlight or the light from a spark was used as the source of light by means of which the phosphorescence could be excited. Screens of variously colored glasses were used in order to find whether the wave length of the exciting light had any effect upon the phosphorescent spectrum. Especially valuable was a glass screen[3] that absorbed all wave lengths except the red, blue and violet. When this was used, no yellow or green light fell upon the phosphorescing uranium salt, so that any light in the yellow and green was necessarily due to phosphorescence

[1] Astrophysical J., **26**, No. 2, Sept., 1907.

[2] Diss., Johns Hopkins University, June, 1908.

[3] This glass screen is very useful for observing Haidinger's brushes. These brushes as seen by the naked eye are yellow and purple. Using a blue glass screen the yellow fringes become dark and show no color. With the above mentioned screen the brushes are red. These facts corroborate the theory given by G. G. Stokes: Collected Papers, **2**, p. 362.

and not to reflection. A Fuess monochromatic illuminator was also used, sunlight or arc light being focused upon the slit of the illuminator. The salt was placed in the beam of transmitted light. Usually the region of spectrum used was 50 or 100 A. U. wide. The phosphorescent light was viewed with the Hilger spectroscope.

In the work on the Zeeman effect, the large electromagnet described by Reese[1] was used. This electromagnet has very large pole pieces. A cell to hold the solution was made of thin cover-glass plates about $1.2 \times 1.2 \times 0.3$ cm. in size. The light from an arc or a Nernst glower was focused upon the solution by means of lenses, and the emergent beam of light focussed upon the slit of the spectroscope.

The concave grating described above was used for mapping the absorption spectra of solutions. A plane Rowland grating was also used for visual work, in the second and third orders of the spectrum. For polarizing the incident light Nicol prisms were used.

When anhydrous salts were employed they were dried in every case by the best methods available. Thus, chlorides were dried in a current of hydrochloric acid, bromides in a current of hydrobromic acid gas, and so on.

The usual precautions were taken in working with non-aqueous solvents to keep out all traces of moisture. Dehydrated salts were, of course, protected from contact with the air.

II. *Absorption Spectra of Potassium Salts in Aqueous Solutions.*

Most potassium salts in solution are colorless, and for this reason it is considered that the potassium atoms do not themselves absorb any light in the visible portion of the spectrum. Several colored potassium salts are known and the color of these are due in some way to the other atoms in the salt molecules. In the present work the absorption spectra of potassium ferricyanide, potassium ferrocyanide, potassium chromate and potassium dichromate have been studied.

Using a 3 mm. length of solution of potassium ferricyanide

[1] Astrophysical J., **12**, No. 2, Sept., 1900.

in water we find that for a normal concentration there is complete absorption of all the shorter wave lengths of light beyond λ 4800. As the concentration is decreased the edge of transmission moves continually towards the violet. It should be noticed that the region between complete absorption and complete transmission for the more concentrated solutions is quite narrow, being less than 40 Angström units, solutions of this salt being thus quite good screens for absorbing light. Continually decreasing the concentration we reach a 0.0156 normal solution, when a transmission band begins to appear. For a certain range of concentration there appears an absorption band in the region λ 4200. Further decrease in concentration results in increasing transmission throughout the violet and ultraviolet. For dilutions greater than 0.00195 normal there is almost complete transmission throughout the ultraviolet. Very faint bands appear in the regions $\lambda\lambda$ 2500 to 2600, $\lambda\lambda$ 2950 to 3050 and $\lambda\lambda$ 3200 to 3250.

Several spectrograms were made of solutions for which the product of concentration and depth of layer were kept constant. In this case the spectrograms will be identical if Beer's law holds. According to this method of testing, Beer's law was found to hold within the ranges of concentration over which the spectrum was mapped.

The absorption of aqueous solutions of potassium ferrocyanide was investigated in the same way. A half-normal solution 3 mm. deep shows that all light of shorter wave length than λ 3950 is absorbed. Keeping the depth of layer the same, it is found that with decrease in concentration the transmission gradually moves towards the ultraviolet, and for dilutions greater than 0.0078 normal there is transmission throughout the whole spectrum. Beer's law was found to hold.

A 2 normal aqueous solution of potassium chromate 3 mm. in thickness shows complete transmission of wave lengths greater than λ 4950. Decreasing the concentration causes the transmission to move gradually towards the violet, and for a 0.01 normal solution a transmission band appears at λ 3100, or, in other words, there appears an absorption band whose center is about λ 3700. As the concentration decreases

this absorption band fills up, the violet edge of the transmission band gradually pushes out into the ultraviolet, and for dilutions greater than 0.0005 normal there is complete transmission throughout the spectrum. Beer's law was found to hold for potassium chromate throughout the above ranges of concentration, except in the more concentrated solutions between 2 normal and 0.25 normal.

Potassium dichromate in water was found to have a much greater absorbing power than the solutions previously described. A one-third normal solution absorbed all wave lengths shorter than λ 5350. As the concentration is decreased the transmission extends farther and farther out into the violet. For a 0.0026 normal concentration a transmission band appears in the violet, thus giving an absorption band whose center is about λ 3800. As the concentration is further decreased transmission becomes greater and greater in the violet and ultraviolet, and is practically complete for a 0.0006 normal concentration. Beer's law has been tested between the above ranges of concentration and has been found to hold.

In photometric measurements to test Beer's law, the equation defining the quantities to be measured is

$$J = J_0 \, 10^{-Acl},$$

where J_0 is the intensity of the light that enters the solution (neglecting any loss due to reflection), J the intensity of the light as it leaves the solution, c the concentration in gram molecules of the salt per liter of solution, l the thickness of layer and A a constant if Beer's law holds. Strictly speaking, the above equation holds for monochromatic light. For ordinary white light one would have to integrate this equation over the range of wave lengths used. The equation would then have the form

$$J = J_0 \int_{\lambda_1}^{\lambda_2} e^{\beta l c} d\lambda.$$

The quantity β is called the index of absorption and A the molecular extinction coefficient. If the absorption is proportionately greater in the more concentrated solutions, then

Beer's law fails and A decreases inversely as the concentration.

From photometric measurements Settegast[1] and Sabatier[2] conclude that the absorption spectrum of potassium dichromate is the same as that of chromic acid, and that the absorption spectrum of potassium chromate is entirely different. This is corroborated by the present work. Settegast finds that Beer's law does not hold for potassium chromate and potassium dichromate, the coefficient A decreasing with increasing concentration. Grünbaum[3] finds the following values of A and ε where $\varepsilon = c/A$:

	Potassium dichromate.	
λ.	Value of A. $c = 0.034.$	Value of A. $c = 0.0034.$
509	62.4	58.0
521	28.7	26.2
536	7.24	6.2

It will be seen that the deviation here from Beer's law is in the opposite direction from that found by Settegast. Grünbaum finds that ε and therefore A depends on the depth of layer.

An example will be given where the same concentration and different depths of the solution were used:

	Value of ε for $c = 0.0034$.		
λ.	25 cm. layer.	12 cm. layer.	5 cm. layer.
521	0.0758	0.0818	0.0884
521	0.0761	0.0830	0.0897

Our work indicates that Beer's law holds for all small concentrations, and usually the deviations for concentrated solutions are very small. Of the potassium salts above described, only potassium chromate between 2 normal and 0.25 normal showed any considerable deviation from Beer's law, and in this case the absorption of the concentrated solution was greater by about 40 Angström units than would be expected if Beer's law held.

[1] Wied. Ann., **7**, 242–271 (1879).
[2] Compt. Rend., **103**, 49–52 (1886).
[3] Ann. Phys., **12**, 1004, 1011 (1903).

The present method is a very good qualitative test of Beer's law, and gives the results for each wave length, whereas most photometric methods only give integrated results over a more or less wide region of wave lengths.

III. *The Absorption Spectra of Uranium Compounds.*

There are quite a large number of spectra of the various compounds and decomposition products of the element uranium. The absorption spectra consist chiefly of the banded spectra of the uranyl and uranous compounds. Uranyl salts in solution are yellow and their absorption spectra consist of a broad band of general absorption in the ultraviolet, which extends more and more into the region of longer wave lengths as the amount of uranyl salt solution in the beam of light is increased. The edge of this absorption band as it gradually advances through the violet and into the blue shows several diffuse bands about fifty Angström units (A. U.) wide and about a hundred A. U. distant from each other. These comparatively fine bands, about twelve in number, are weak, having very diffuse edges, and can be photographed only when they lie near the edge of the general absorption band. Among those who have carried out investigations upon the absorption spectra of these compounds may be mentioned: H. Oeffinger,[1] H. Becquerel,[2] W. Boehlendorff,[3] O. Knoblauch,[4] E. Deussen,[5] Formánek,[6] Hartley,[7] Houstoun and Russel,[8] Jones and Strong,[9] and others.

In the discussion of the uranyl bands it will be found convenient to designate them by the letters *a*, *b*, *c*, *d*, etc., the band *a* being of the greatest wave length, and the wave lengths of the other bands gradually decreasing. In general it will be found that this classification is very useful and upon general observations it might be supposed that each band had

[1] Ueber die Lichtabsorption der Uransalze, Inaug. Diss., Tübingen, 1866.
[2] Ann. Chim. Phys., [6] **14**, 170–257 (1888).
[3] Inaug. Diss., Erlangen, 1890.
[4] Wied. Ann., **43**, 738–783 (1891).
[5] *Ibid.*, **66**, 1128–1148 (1898).
[6] Die qualitative Spectralanalyse anorg. Körper, Berlin, 1900.
[7] J. Chem. Soc., **83**, 221–246 (1903).
[8] P. Roy. Soc. Edinb., **29**, II, 68.
[9] Physik. Z., **10**, 499 (1909).

its origin in a particular vibration of the vibrating system. But at low temperatures these bands are found to consist of a number of much finer bands, and the absorption spectra become very complicated indeed, so that it is clear that changes which are observed at ordinary temperatures may be due to relative changes in the groups of five bands composing the larger bands, *a, b, c, d,* etc. For instance, shifts in the position of the bands, *a, b, c,* etc., due to relative changes in the intensity of the components, may be observed when the frequency of none of the component bands has been changed at all.

Becquerel[1] found that the position and intensity of the absorption bands of a crystal depend on the direction in which the light traversed the crystal. To study this phenomenon of absorption he cut sections of crystals in three different directions. One section was cut parallel to the optic axes that cut each other obliquely ("Axe moyen"), one section perpendicular to the bisector of the acute angle ("bissectrice aiguë") and another section perpendicular to the bisector of the obtuse angle ("bissectrice obtuse"). Crystals of uranyl nitrate belong to the orthorhombic type. Becquerel measured the wave lengths of the three bands, *a, b, c,* for the different sections.

Uranyl Nitrate.

	a.	*b.*	*c.*
Bissectrice aiguë	λ 4870 to λ 4840	λ 4725 to λ 4666	λ 4568 to λ 4525
Axe moyen	. . . .	λ 4698 to λ 4660	λ 4555 to λ 4520
Bissectrice obtuse	λ 4864	λ 4695	λ 4551

The wave lengths of the absorption bands of crystals of the double chloride of uranyl and potassium were as follows:

Bissectrice aiguë	. . . .	λ 5007	λ 4957		λ 4905
Axe moyen	. . . .	λ 5000	λ 4935 to 4920		. . . .
Bissectrice obtuse	λ 5047	λ 5000	λ 4953 to 4910		. . . .

Bissectrice aiguë	. . . .	λ 4843	λ 4783	λ 4741	. . . .
Axe moyen	λ 4869	. . . .	. . . .	λ 4741	λ 4702
Bissectrice obtuse	λ 4869	λ 4826	λ 4783	λ 4741	λ 4702

[1] *Loc. cit.*

Knoblauch[1] investigated the effect of change of concentration on the absorption spectra of various uranyl salts. He kept the amount of salt in the path of the beam of light constant but varied the concentration between wide limits. In the case of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, he compared the absorption of solutions having concentrations about 1.1 normal (c_1) and 0.0033 normal (c_2) $(c_1 : c_2 = 3428 : 1)$. If the molecules of uranyl nitrate had acted like the molecules of a gas the concentrated solution would have exerted a pressure of 25.4 atmospheres and the dilute solution $1/_{136}$ atmosphere. For both solutions the a (λ 4920–4850) and the b (λ 4780–4680) bands appeared in the same position. With uranyl acetate, $UO_2(C_2H_3O_2)_2 2H_2O$, a change in concentration of $c_1 : c_2 = 446 : 1$ did not cause any shift in the a (λ 4940–4870) or the b (λ 4820–4730) bands. The position of the edge of the ultraviolet absorption was the same for both concentrations. The absorption bands were found to be more intense for the dilute solution. Uranyl chloride in concentrations $c_1 : c_2 = 2500 : 1$ showed three absorption bands a (λ 4950–4870), b (λ 4820–4720) and c (λ 4650–4560). The bands were unaffected by dilution.

Knoblauch considers that deviations from Beer's law must be due to (1) a change in the molecular complex that constitutes the absorber; (2) a chemical change such as hydrolysis or hydration; (3) dissociation; (4) mutual actions which exist between the dissolved molecules in concentrated solutions that do not occur in very dilute solutions. The experimental results which he obtains for uranyl and eosin salts indicate that deviations from Beer's law cannot be explained as being due to dissociation.

Deussen[2] has made a very complete examination of the absorption spectra of various uranyl salts in different solvents and in mixtures of different solvents. Below are the wave lengths measured by Deussen:

[1] *Loc. cit.*
[2] *Ibid.*

Uranyl Nitrate.

Solvent.	a.	b.	c.	d.	e.
Water	4860	4720	4540	4380	4290
Ethyl alcohol	4845	4680	4490	4360	4240
Methyl alcohol	4850	4680	4490	4360	4295
Acetone	4845	4680	4490	4360	4240
Glycerol	4870	4735	4525	4350	4220
Amyl alcohol	4845	4680	4490	4360	4240
Acetic ester	4850	4685	4495	4365	4250
Ether	4850	4685	4495	4370	4255
	f.	g.	h.	i.	j.
Water	4150	4020	3870	3790	3690
Ethyl alcohol	4090	3990	3840	3750	3660
Methyl alcohol	4050	4000	3840	3750	3660
Acetone	4090	3990	3855	3760	3670
Glycerol	4060	3910	3820	3710	. . . .
Amyl alcohol	4090	3990	3840	3750	3660
Acetic ester	4095	3995	3845	3755	3665
Ether	4100	4000	3850	3760	3670

The above wave lengths of the bands do not agree very well with our own measurements. For instance, the ethyl alcohol bands are found to have a greater wave length than the water bands. Deussen worked with mixtures of all the above solvents and water. He obtained some very remarkable results. For example, he finds that, as compared with a pure aqueous solution of uranyl nitrate, in the 50 per cent. ethyl alcohol solution all the uranyl bands are shifted towards the red. When the solvent contains 80 per cent. alcohol all the bands are shifted towards the violet, and for a pure alcohol solution all the uranyl bands are of shorter wave length than for a pure water solution.

Deussen obtained very interesting results for uranyl nitrate in mixtures of water and glycerol. As the percentage of glycerol increases the *c* and *d* bands broaden and finally, for a pure glycerol solution, form but a single band. At the same time all the other bands are shifted towards the red.

Uranyl Chloride.

Solvent.	a.	b.	c.	d.	e.	f.
Water	4900	4735	4580	4410	4285	4140
Ethyl alcohol	4910	4745	4595	4425	4305	4200
Glycerol	4920	4755	4600	4510	4410	4280

Uranyl Chloride—(Continued).

Solvent.	g.	h.	i.	j.	
Water	4025	3925	3800	3710	. . . .
Ethyl alcohol	4080	3990	3870	3750	. . . .
Glycerol	4170	4030	3940	3810	3715

For uranyl chloride solutions in mixtures of water and glycerol, Deussen finds that the *c* band of the water solution breaks into two bands when the solvent is pure glycerol. Increasing percentages of glycerol cause an increased shift of the bands towards the red.

Uranyl Sulphate, $UO_2SO_4.3H_2O$.

Solvent.	a.	b.	c.	d.	e.	f.	g.	h.
Water	4885	4725	4560	4410	4310	4180	4060	3950
Ethyl alcohol	4890	4730	4565	4420	4320	4190	4070	3960
Glycerol	4890	4730	4570	4430	4340	4210	4090	3980

H. Becquerel[1] has made a number of observations on the absorption spectra of uranium compounds at low temperatures. He considers that the absorption and phosphorescent bands are parts of a single system. They have two bands in common. He states that any modification in the appearance of one set of bands for any compound is reproduced by a similar change in the other set of bands. In general, the bands found at the temperature of liquid air are moved towards the violet with respect to the same bands at ordinary temperatures. Uranyl nitrate, at ordinary temperatures, gives wide diffuse bands whose intensities come at about their middle. At the temperature of liquid air each group is resolved into several bands, and the most intense of these bands are towards the violet. A table of the wave lengths of these bands is given below.

Bois and Elias[2] find that the double sulphate of uranyl and potassium when cooled to —190° C. gives bands at $\lambda\lambda$ 4878, 4882, 4888 and 4905. These seem to broaden slightly when placed in a strong magnetic field. At 18° C. uranyl nitrate gave bands at λ 4675–4716, λ 4849–4880, and at —190° C. strong bands at λ 4679–4697, λ 4845–4849 and λ 4853–4857.

[1] Compt. Rend., **1885**, 1252; **1907**, 459, 671.
[2] Ann. Phys., **1908**, 299.

Crystals of Uranyl Nitrate.		Double Sulphate of Uranyl and Potassium.		Double Chloride of Uranyl and Potassium.	
Room temperature. Diffuse band	Liquid air.	Room temperature.	Liquid air.	Room temperature.	Liquid air.
6201–6150	6360		6500	6400–6360	6360
	6170(s)		6270	6315	
	6145–6127	6155 Weak	6185–6175		
			6155–6145(s)		
	6104	6039–5945	6039–5945	6055	6030(s)
	6050		5910(f)	5970–5975	5800
	5856(s)	5890–5885	5887(s)	5920	
	5833(s)		5830		5751(s)
	5782		5763	5776–5740(s)	5721(f)
	5707	5760	5715	5702(f)	
	5630		5695–5674	5632(t)	5619(f)
	5600		5647(s)		5555(f)
	5580(s)		5616(s)	5515–5481(s)	5535
	5553(s)	5610–5560	5591(s)	5447	5486(s)
	5490		5486		5462(f)
	5435	5535	5410		5435(t)
	5375	5515	5427(t)	5394(f)	5400(f)
	5323(s)		5384(f)		5373(f)
	5297(s)		5365(s)		5361(f)
	5272		5347	5275–5247(s)	5315(f)
	5240		5338(s)		5295(s)
	5190		5334	5205	5224(s)
	5137		5138	5161(f)	5202(f)
5120–5060	5115		5124(f)	5116(f)	5196(f)
	5093(s)		5114(s)	5080(t)	5156(f)
	5072(s)		5000	5065(t)	5072
	5018		4932(s)	5042	5040(s)
	4975		4910(s)	4995	5012
	4925				4990(f)
4893–4855	4900(s)				

Uranous salts are of a deep green color and have a very characteristic absorption spectrum, which consists of diffuse bands scattered throughout the spectrum. With the exception of a short description of a few of the bands by Formánek practically nothing has been done on the absorption of uranous salts either in solution or in the crystalline condition.

IV. The Absorption Spectrum of Uranyl Chloride.

The absorption spectrum of uranyl chloride (crystals having the composition $UO_2Cl_2.H_2O$ at ordinary temperatures) has been mapped for solutions in water, methyl and ethyl alcohols, in mixtures of these solvents and in solutions with aluminum and calcium chlorides and for the anhydrous salt.

(a) *Uranyl Chloride in Aqueous Solutions.*—The absorption spectrum of uranyl chloride in water was mapped for 1, 0.75, 0.50, 0.33, 0.25, 0.16 and 0.125 normal solutions, the depth of layer being 3 mm. and the time of exposure to the Nernst glower with a current of 0.8 ampere being 1 minute. The slit width was 0.08 mm.

The absorption spectra of the chloride and bromide are very similar, the blue-violet absorption band being slightly stronger for the chloride. The uranyl bands are very broad and diffuse for both salts, being slightly more diffuse for the chloride. Practically only the *a*, *b* and *c* bands appear with any strength.

Of these, *a* and *b* are the stronger. They appear of about the same intensity and are about 80 A. U. wide. For the bromide *a* is considerably weaker than *b*. The sulphate and nitrate, on the other hand, show practically all of the uranyl bands, the bands being the strongest in the sulphate solution. In this salt solution the *b* and *c* bands are six to ten times as strong as the *a* band. In the nitrate this difference is not so marked, and the bands appear somewhat finer than in the case of any other salt. The acetate shows the greatest absorption of all the salts mentioned above. Here, the *a*, *b* and *c* bands are very faint. About half a dozen very faint bands appear together.

For the 1 N solution the ultraviolet and blue-violet bands merge together and end at λ 4550. For the 0.75 N solution the blue-violet band is limited by regions of absorption beyond the limits $\lambda\lambda$ 4500 and 3900, for the 0.5 N solution, $\lambda\lambda$ 4470 and 3950, and for the 0.33 N solution, $\lambda\lambda$ 4400 and 4050, the center of the band thus being at λ 4200. Collecting the results of their measurements of the center of this blue-violet band we have:

Uranyl chloride	λ 4200
Uranyl nitrate	λ 4150
Uranyl bromide	λ 4250
Uranyl acetate	λ 4200
Uranyl sulphate	λ 4180

Therefore, for all these salts, the blue-violet bands appear at the same position.

The band also widens with increase of concentration quite uniformly. The edges of the ultraviolet band are: 0.75 N λ 3700, 0.5 N λ 3670, 0.33 N λ 3650, 0.25 N λ 3630, 0.16 N λ 3600, and 0.125 N λ 3570.

The positions of three of the uranyl bands (a, b and c) were measured. On account of the extreme faintness of c the result for this band is not very accurate.

$a.$	$b.$	$c.$	$d.$	$e.$	$f.$	$g.$
4920	4740	4560	4460	4315	4170	4025

In addition to the bands already given, uranyl chloride has several remarkably fine bands in the green. These bands are not more than 5 A. U. wide and were first seen on spectrograms made on the Wratten and Wainwright red-sensitive films. They appear only for aqueous solutions of uranyl chloride. The addition of calcium or aluminium chloride causes them to disappear. They do not appear in the alcoholic solutions. Uranyl sulphate shows the same bands at about the same position as the chloride but much weaker—too weak to be separa ted. The wave lengths are as follows:

$\lambda\lambda$ 5185, 5200, 6000, 6020, 6040 and 6070.

So far as the writers know, this is the first time that these bands have been noticed in aqueous solutions. Uranyl salts

give a spectrum of emission through phosphorescence, and this spectrum appears to be a continuation of the absorption spectra to longer wave lengths. Becquerel[1] has shown that any uranyl compound showing a modification of the absorption bands shows a similar modification of the emission phosphorescent bands.

A series of spectrograms was made to test Beer's law. Exposures were made under the standard conditions with 1, 0.75, 0.5, 0.33, 0.25, 0.16, 0.125 normal solutions of uranyl chloride, the corresponding depths of cell being 3, 4, 6, 9, 13, 18 and 24 mm.

There is a slight transmission band in the ultraviolet between the blue-violet and ultraviolet bands. This transmission region is roughly 100 A. U. wide, and is so faint that it does not appear upon the printed plates. This band obeys Beer's law. The long wave length edge of the blue-violet absorption band, however, deviates slightly from Beer's law. For the 1, 0.75, 0.5 and 0.33 normal solutions the absorption is slightly greater than for the 0.25 normal solution. The 0.25, 0.16 and 0.125 normal solutions obey Beer's law. The edge for the 1 normal solution is roughly 75 A. U. nearer the red than for the 0.25 normal solution. The uranyl bands *a* and *b* are slightly stronger for the more concentrated solutions. A similar run for Beer's law was made between the concentrations 0.125 and 0.0156 normal. Beer's law holds in this case, the absorption being complete for wave lengths less than $\lambda\,4150$. The uranyl bands do not appear at all.

(b) *Uranyl, Calcium and Aluminium Chlorides in Water.*— Spectrograms were taken of aqueous solutions of uranyl chloride of a constant concentration to which varying amounts of calcium chloride were added. The addition of calcium chloride causes the ultraviolet, the blue-violet and the uranyl bands to widen generally. The effect upon the uranyl bands is, however, very small. The effect of aluminium chloride, on the other hand, is very great. The two narrow and faint bands at $\lambda\,5200$ appear only in the pure aqueous

[1] Mém. Acad. Sci., **40**, 1872.

solution of uranyl chloride. The *a* band in the aqueous solution is about 60 A. U. wide, and is almost as intense as the *b* band. The addition of aluminium chloride causes the band to become quite narrow, about 25 A. U. wide. A slight addition of aluminium chloride decreases the intensity of the band very considerably. Further increases in the amount of aluminium have very little effect. The addition of aluminium chloride also causes the bands to shift to the red, the shifts in some instances amounting to 25 A. U. The intensity of the *b* and *c* bands is very greatly increased by the addition of aluminium chloride; and by making the solution about 2 normal with aluminium chloride these bands are shifted about 30 A. U. to the red as compared with the same bands for the pure uranyl chloride solution. The *d*, *e*, *f*, *g* and *h* bands are also increased in intensity, but are but very slightly shifted to the red. The *d* and *e* bands are widened so that they form practically a single band.

(c) *Uranyl Chloride in Methyl Alcohol.*—The first spectrogram for mapping out the absorption spectrum of uranyl chloride in methyl alcohol is given in B, Plate I. Exposures were made to the Nernst glower for 1 minute with a slit width of 0.08 mm. and a current of 0.8 ampere. The depth of cell is 6 mm. for each strip. Beginning with the strip nearest the numbered scale the concentrations are 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2 and 0.25 normal.

The alcoholic solution of uranyl chloride is very similar to the alcoholic solution of uranyl nitrate, the absorbing power of both solutions being considerably greater than that of aqueous solutions. The aqueous solution of uranyl chloride shows only a few of the characteristic uranyl bands in its absorption spectrum. In the alcoholic solution, however, they appear very strongly.

Starting with the most concentrated solution, whose absorption spectrum is given by the strip furthest from the numbered scale, we have the bands *a* and *b* appearing and all wave lengths less than $\lambda\,4500$ completely absorbed. The *b* band is very strong, the *a* band very weak—almost lost in this region of the spectrum where the film is less sensitive to the light.

For the next concentration, 2 N, we have a weak transmission band appearing in the ultraviolet. Other uranyl bands appear as the concentration is decreased. We shall now consider the blue-violet band. For the o.2 N solution its limits are $\lambda\lambda$ 4450 and 3800, for the o.158 N solution $\lambda\lambda$ 4400 and 3900, and for the o.125 N solution $\lambda\lambda$ 4350 and 3900. The middle of the band would thus come at about λ 4100.

The uranyl bands a, b, c, d, e, f, g, h, i and j all appear. The bands b and c are the largest and strongest. Band a is relatively much weaker. The appearance of the bands is somewhat like the bands of uranyl nitrate in methyl alcohol. The uranyl nitrate bands are on the whole considerably fainter and narrower than the uranyl chloride bands. Bands a, b and c are almost of the same intensity in the case of the nitrate, all being quite faint. The blue-violet band is much more diffuse in the spectrum of the uranyl nitrate. The following are the wave lengths of the bands of uranyl chloride, the second row giving the wave lengths of the same bands for uranyl nitrate in methyl alcohol:

	a.	b.	c.	d.	e.
Chloride	4930	4760	4610	4465	4345
Nitrate	4930	4760	4610	4460	4325

|	f.	g.	h.	i.	j.
Chloride	4220	4090	3980	3860	3760
Nitrate	4190	4070	3970	3855	....

The a, b and c bands of the chloride and nitrate come at about the same positions, but the e, f, g and h bands of the chloride are all shifted towards the red as compared with the same bands of the nitrate. The uranyl chloride bands in water are slightly shifted towards the violet with reference to the uranyl chloride bands in methyl alcohol.

The relative intensities of the bands do not completely agree with those given by Deussen.[1] In the main, the results agree fairly well with his, he finding that in alcohol the bands are shifted towards the red.

A plate was made in exactly the same way as B, Plate I, the only difference being that the depth of cell was 15 mm.

[1] Ann. Phys., **66**, 1137 (1898).

Plate I.
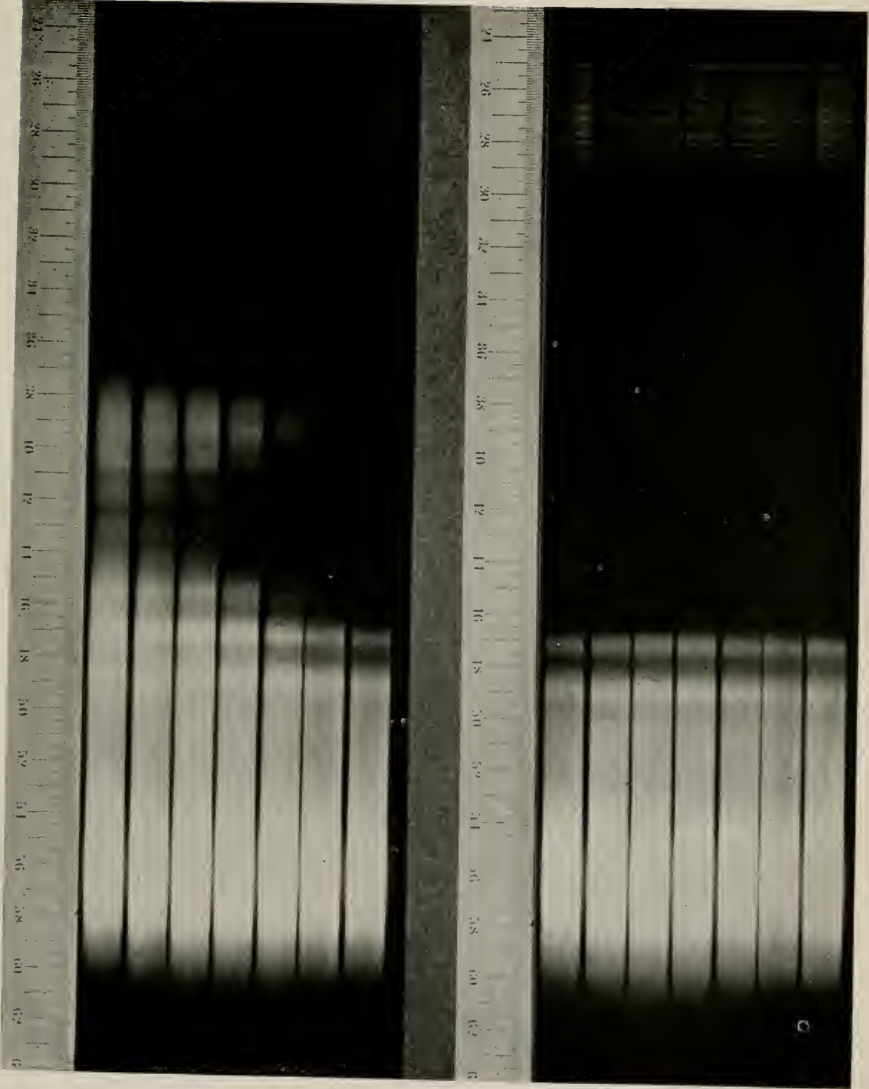
whereas for the spectrogram previously described the depth of cell was only 3 mm. This spectrogram shows very well how a uranyl band increases in intensity as the edge of the blue-violet band approaches it.

The a band thus increases in intensity and in width with increase of concentration. The band also seems to widen un-symmetrically, although the disymmetry may be due in part to the unequal sensitiveness of the photographic film to different wave lengths of light in this part of the spectrum.

The spectrogram A, Plate I, taken to test Beer's law, was made by exposures of 1 minute to the Nernst glower with a current of 0.8 ampere, and slit width of 0.08 mm. Exposures to the spark in order to get reference lines were made only in the ultraviolet. Starting with the strip next to the numbered scale, the concentrations were 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2 and 0.25 normal, the corresponding depths of cell being 24, 19, 15, 12, 9.5, 7.5 and 6 mm.

Beer's law holds for the alcoholic solutions between 0.25 N and 0.06 N. The limit of absorption is at λ 4650 and is quite sharp, this being the long wave length edge of the uranyl c band. The b band is very strong, the a band quite weak.

A very faint transmission band appears at λ 3850 and is about 100 A. U. wide. This band also obeys Beer's law and is, in fact, quite a sensitive index for any deviations from this law.

(d) *Absorption Spectrum of Anhydrous Uranyl Chloride.*— The absorption spectrum of the anhydrous chloride was photographed in the same way as that of the anhydrous nitrate. The bands differ considerably from the bands of the aqueous solution, and one cannot tell very well whether they are identical with the corresponding a, b, c, etc., bands of the solution or not. Their wave lengths are approximately as follows: $\lambda\lambda$ 4950 (narrow), 4860, 4765, 4700, 4615, 4540, 4460, 4320, 4290, 4160, 4050 and 3940.

(e) *Absorption Spectrum of Uranyl Chloride in Methyl Alcohol and Water.*—A spectrogram was made of a solution of uranyl chloride of constant concentration in mixtures of methyl alcohol and water. A small addition of water causes

a considerable decrease in the absorption power of the uranyl
chloride.   When the amount of water has reached about 16
per cent. very little further change is produced by further in-
creasing the amount of water.   The most important effect
of the addition of water is the effect upon the uranyl bands.
For a pure alcoholic solution the *a* and *b* bands appear, the *b*
band being quite intense.   Addition of water causes both
a and *b* to decrease in intensity and apparently to shift to-
wards the violet.   A spectrogram for a solution of smaller
concentration shows the *a*, *b*, *c*, *f*, *g*, *h* and *i* bands; the solu-
tion containing 8 per cent. water the *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j*
bands; the 16 per cent. water solution *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j*;
the 24 per cent. water solution shows all these bands greatly
weakened; and in solutions containing a greater amount of
water practically only the *b* and *c* bands appear, and these
are very diffuse.   The general effect upon the positions of
the bands is quite remarkable, the *b* and *c* bands apparently
being shifted to the violet with increase of water, whereas
the ultraviolet bands appear to be shifted towards the red.

(*f*) *Absorption of Uranyl Chloride in Ethyl Alcohol.*—The
absorption spectrum of uranyl chloride in ethyl alcohol shows
the uranyl bands quite strongly, although they are less in-
tense than for the methyl alcohol solution.   A very inter-
esting resemblance has been found for the various uranyl
bands of different mixtures.   The absorption spectrum of a
solution of uranyl chloride in ethyl alcohol has been found to
be almost the same as that of a methyl alcohol solution of uranyl
chloride containing a 0.9 normal concentration of calcium
chloride, or of an aqueous solution of uranyl chloride and a 2
normal concentration of aluminium chloride.

The positions of the uranyl bands for the ethyl alcohol
solution are approximately:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
λ	4900	4750	4580	4400	4400	4250	4100	3980	3860

The relation above mentioned comes out much better on
comparing the spectrograms.   The values of wave lengths
thus far given do not bring this out very well on account of

the difficulty of making measurements. Much more work is to be carried on along this line, and the measurements above given are to be considered as more or less of a preliminary character.

(g) *Uranyl Chloride and Calcium Chloride in Methyl Alcohol.*—*Plate II, A and B.*—These spectrograms, showing the absorption spectra of mixtures of uranyl chloride and calcium chloride in methyl alcohol, were taken under the same conditions. Exposure was made to the Nernst glower for 1 minute with a slit width of 0.08 mm. and a current of 0.8 ampere. The ultraviolet standard lines were photographed with the uranyl solution removed from the light beam. In every case the concentration of uranyl chloride was 0.125 normal. Starting with the strip at the top of the spectrogram of both A and B the concentrations of calcium chloride were 0.0, 0.144, 0.0288, 0.432, 0.576, 0.72 and 0.9 N. In A the depth of solution was 6 mm, in B 3 mm.

The effect of calcium chloride on the absorption spectra of a methyl alcohol solution of uranyl chloride is very slight, notwithstanding the power of calcium chloride to combine with alcohol. An increased amount of calcium chloride causes the ultraviolet and blue-violet bands to widen slightly, as will be seen from both A and B. The change in the intensity of the uranyl bands is also very slight.

In the upper strip of B appear the bands a, b, c, d, e, f, i and j. Only one edge of a is to be seen clearly; b and c are clear and entirely separated; d is very diffuse and especially so on the violet side; e is also diffuse, but is a distinct band. f, g and h are distinct and entirely separated; i and j can also be noticed. When calcium chloride is added a very peculiar phenomenon takes place. The bands d and e come together and, as far as one can tell, form a single band. This causes the bands f, g and h to shift to the red, the other bands becoming too faint to be recognized. Measurements gave the following wave lengths for the solution of uranyl chloride in methyl alcohol itself: b, λ 4760; c, λ 4590; d, λ 4465; e, λ 4345; f, λ 4225; g, λ 4095; h, λ 3975; and i, λ 3860. Taking up the solution containing a 0.9 normal concentration of calcium

chloride we find that the *b* and *c* bands have remained at the same part of the spectrum. The *d* and *e* bands have combined into one large diffuse band whose position is approximately λ 4420. The *f*, *g* and *h* bands are now at $\lambda\lambda$ 4260, 4120 and 4010, respectively.

A spectrogram was also taken under conditions identical with those in A and B in every respect except that the depth of layer was made 15 mm. Here only the *a* and *b* bands appeared. The *b* band was very wide and strong, the *a* band very weak. In the pure uranyl chloride solution the *a* band was quite wide. As the amount of calcium chloride was increased the band became much narrower and its center shifted from λ 4925 for the pure uranyl chloride solution to about λ 4895 for the solution containing a 0.9 normal concentration of calcium chloride. Whether this could be accounted for as due entirely to unsymmetrical narrowing is uncertain, though it seemed that its short wave length edge was slightly shifted towards the violet.

V. *Absorption Spectrum of Uranyl Nitrate under Different Conditions.*

(*a*) *Uranyl Nitrate in Aqueous Solution.*—The spectrum of uranyl nitrate in water is a typical example of the uranyl salts. With a depth of solution of 3 mm. its absorption spectrum was investigated between concentrations of 1.5 normal to 0.0234 normal. For the 1.5 normal solution the absorption consists of a band in the blue-violet and absorption throughout the ultraviolet portion of the spectrum. As the concentration decreases the blue-violet band fills up with transmission, and the ultraviolet absorption is pushed farther and farther out into the ultraviolet. The blue-violet band is practically gone at a concentration of 0.5 normal, and there is almost complete transmission throughout the ultraviolet for concentrations less than 0.02 normal.

During these changes in concentration a large number of bands about 50 A. U. wide make their appearance. Near the edge of an absorption band these bands are relatively quite clear. As the absorption edge recedes from the uranyl bands,

Plate II.

B   A
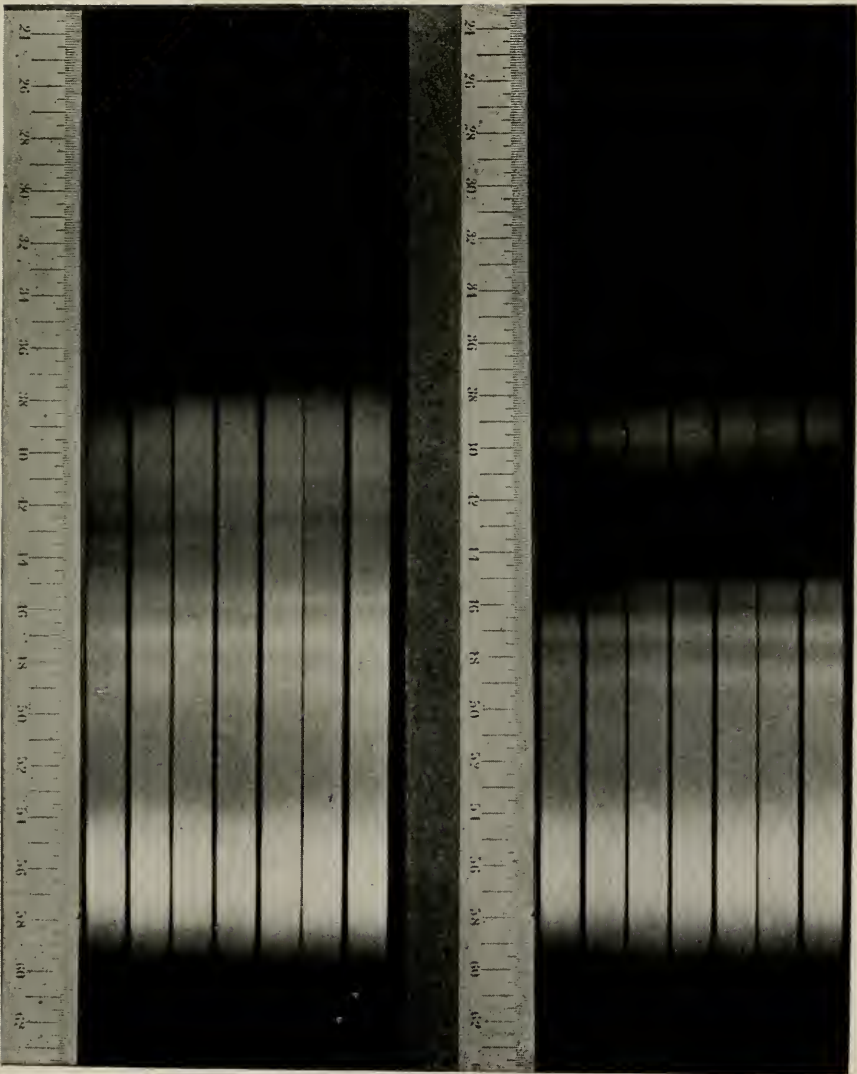
the general transmission is so great as to obscure them almost completely.

A, Plate IV, represents the absorption spectra of an aqueous solution of uranyl nitrate of different depths of layer. The narrow and rather weak bands shown here are the uranyl bands. Twelve of these bands have been photographed. Starting at the band of longest wave length they will be designated by the letters *a*, *b*, *c*, *d*, etc. On account of the irregularity of the distribution of light in the spark spectrum and the small intensity of the uranyl bands, the Nernst glower was used as the source of light in the ultraviolet, and long exposures were made. A screen was used that cut out all wave lengths greater than λ 4200. A represents a typical spectrogram of this kind. Starting with the spectrum strip at the top, the concentrations were 1.5, 1.1255, 0.75, 0.5, 0.375, 0.25 and 0.1875 N. The slit width was 0.08 mm. and the current through the Nernst glower 0.8 ampere. The spectra of wave lengths greater than λ 4300 represent the absorption of a depth of layer of 15 mm.; the spectra of shorter wave lengths represent the absorption of a depth of layer of 3 mm. The upper spectrum strip represents then the absorption spectrum of a 1.5 normal solution of uranyl chloride 15 mm. thick, exposure to the Nernst glower having been 1 minute. It will be seen that the uranyl band *a* comes out very strongly. The screen was then placed in the path of light and exposure of 5 minutes made to the violet and ultraviolet beyond λ 4300, a solution of uranyl nitrate of 1.5 normal concentration and 3 mm. deep being in the path of the beam of light. This amount of uranyl nitrate absorbed practically all the light in this region. A very short exposure was afterwards made to the spark in the region λ 2600, in order to get a comparison spark spectrum in this region so that the wave lengths of the uranyl bands could be measured.

Throughout this work a comparison spark spectrum usually containing the very strong line λ 2478.8 was photographed on each spectrum strip. In measuring the uranyl bands all measurements were made from this line as a standard, and although the absolute wave lengths of the uranyl bands may

not be correct to within 20 A. U., yet relatively they are probably correct to within less than 10 A. U. for the finer bands.

The second spectrum strip from the top represents in the long wave length end of the spectrum the absorption of a 15 mm. layer of a 1.125 normal solution of uranyl nitrate exposed 1 minute to the Nernst glower. The a band appears, although not nearly as intense as in the spectrum strip above. The region of shorter wave lengths beyond λ 4300 represents the absorption of a 3 mm. layer of a 1.125 normal solution exposed 5 minutes to the Nernst glower. A very faint transmission is shown in the region λ 3700. The ultraviolet line λ 2478.8 is shown in the comparison spark spectra. The other spectrum strips were made in a similar manner, with the concentrations given above.

By this method of exposing two new bands were detected in the ultraviolet. In aqueous solutions the intensities of the bands are much the same. In other solvents, however, and for other uranyl salts, the relative intensities of the bands change very greatly. For uranyl nitrate crystals the bands are even more closely related to each other than in aqueous solutions. The longer the wave length of the band the more intense and wide it is as a rule. The position of the long wave length bands in the orthorhombic uranyl nitrate crystals, $UO_2(NO_3)_2 6H_2O$, is the same as the position of the bands for an aqueous solution. The wave lengths of the bands are as follows:

	a.	b.	c.	d.	
Water sol.	4860	4720	4540	4380	Deussen.
Water sol.	4870	4705	4550	4390	Jones and Strong.
Crystals	4870	4705	4500–4565	4405	

	e.	f.	g.	h.	
Water sol.	4290	4150	4020	3870	Deussen.
Water sol.	....	4155	4030	3905	Jones and Strong.
Crystals	4275	4170	4050	3935	

	i.	j.	k.	l.	
Water sol.	3790	3690	....	....	Deussen.
Water sol.	3815	3710	3605	3515	Jones and Strong.
Crystals	3830	(3720?)	3600		

In the original film from which A, Plate I, was made all
these bands except *d* could be very distinctly seen. The
bands of longer wave length are slightly wider. The *i* band
is considerably weaker than its neighboring bands.

(*b*) *Absorption Spectrum of Uranyl Nitrate Crystals.*—For
the aqeuous solution there is no sign that the bands can be
broken up. In the crystal spectrum this is not the case.
The *a* band is narrow. The *b* band is also very narrow, about
15 A. U. wide. A very faint band appears about λ 4650.
The *c* band, on the other hand, is very wide, about 70 A. U.,
and is probably double. The *d* band is about 50 A. U. wide,
and the *e* band is about 70 A. U. wide and appears double.
The *f* band is the most intense and is about 40 A. U. wide.
The bands *g, h, i* and *j* keep decreasing in intensity respectively.
The above description is of a spectrogram taken of a crystal
in Canada balsam, and of course the width of the bands
varies with the time of exposure and various other things.
The above spectrogram showed many details, however, that
other spectrograms did not. It will thus be seen that the
a, b, c, d, j and *k* bands of the solution agree fairly well with
those of the crystal, and that the crystal bands *f, g, h* and *i*
are shifted towards the red with reference to the bands in the
aqueous solution.

(*c*) *Effect of Dilution upon the Uranyl Bands.*—The effect of di-
lution on the position and intensity of the blue-violet, the ultra-
violet and the uranyl bands of the acetate, nitrate and sulphate
of uranyl in water was tried. The absorption spectra of solutions
about 1 normal and 3 mm. deep were photographed along by
the side of the absorption spectra of 0.008 normal solutions of
the same salts 380 mm. deep. The absorption consisted of
the blue-violet band, the ultraviolet band and the *a, b, c,
i, j* and *k* bands. Between the blue-violet and ultraviolet
bands there was the transmission band containing *i, j* and *k*.
For each of the three salts this transmission band was much
weaker for the dilute solution, whereas in the cases of the sul-
phate and nitrate the long wave length transmission edge of
the blue-violet band was stronger for the more dilute solu-
tion. The opposite was true of the acetate solution. In the

dilute solution of the acetate the bands were more intense than for the more concentrated solution. There was no noticeable change in the position of the bands. Neither the intensity nor the position of the uranyl nitrate or the uranyl sulphate bands was changed by the above dilution.

A, Plate III, represents the spectrogram comparing the spectra of the same amount of uranyl salt in a concentrated and in a dilute solution. Starting with the strip adjacent to the numbered scale we have the absorption spectra of a 1.1 normal solution of uranyl nitrate in water, the depth of the cell being 3 mm. The next spectrogram is of the same solution. Then distilled water was poured into the solution until the length of column was 380 mm. The absorption spectrum of this solution is given in the third strip. The fourth strip represents the absorption of a 0.75 normal solution of uranyl sulphate, the depth of cell being 4 mm. The fifth strip is for the same solution diluted until the depth was 380 mm. The sixth strip represents the absorption of a 0.188 normal solution of uranyl acetate 14 mm. deep. The last strip is for the same solution diluted to a depth of 380 mm.

A more detailed study was made as to whether Beer's law holds for uranyl nitrate and for the other uranyl salts. The method of taking the spectrograms is the same as that used for the potassium salts.

Beer's law was found to hold for dilute solutions of uranyl nitrate in water. When the concentration is greater than 0.5 normal the absorption is greater than it should be if Beer's law held.

(d) *Uranyl Nitrate in Methyl Alcohol.*—In methyl alcohol the general appearance of the absorption is very similar to that of the aqueous solution, the blue-violet, the ultraviolet and uranyl bands appearing under the same general conditions as for aqueous solutions. There is a very marked deviation from Beer's law for the more concentrated solutions, however, the absorption being greater than it would be if Beer's law held. The position of the bands are quite different from the positions of the uranyl bands of the aqueous solution, or of the crystals, as shown by the following values:
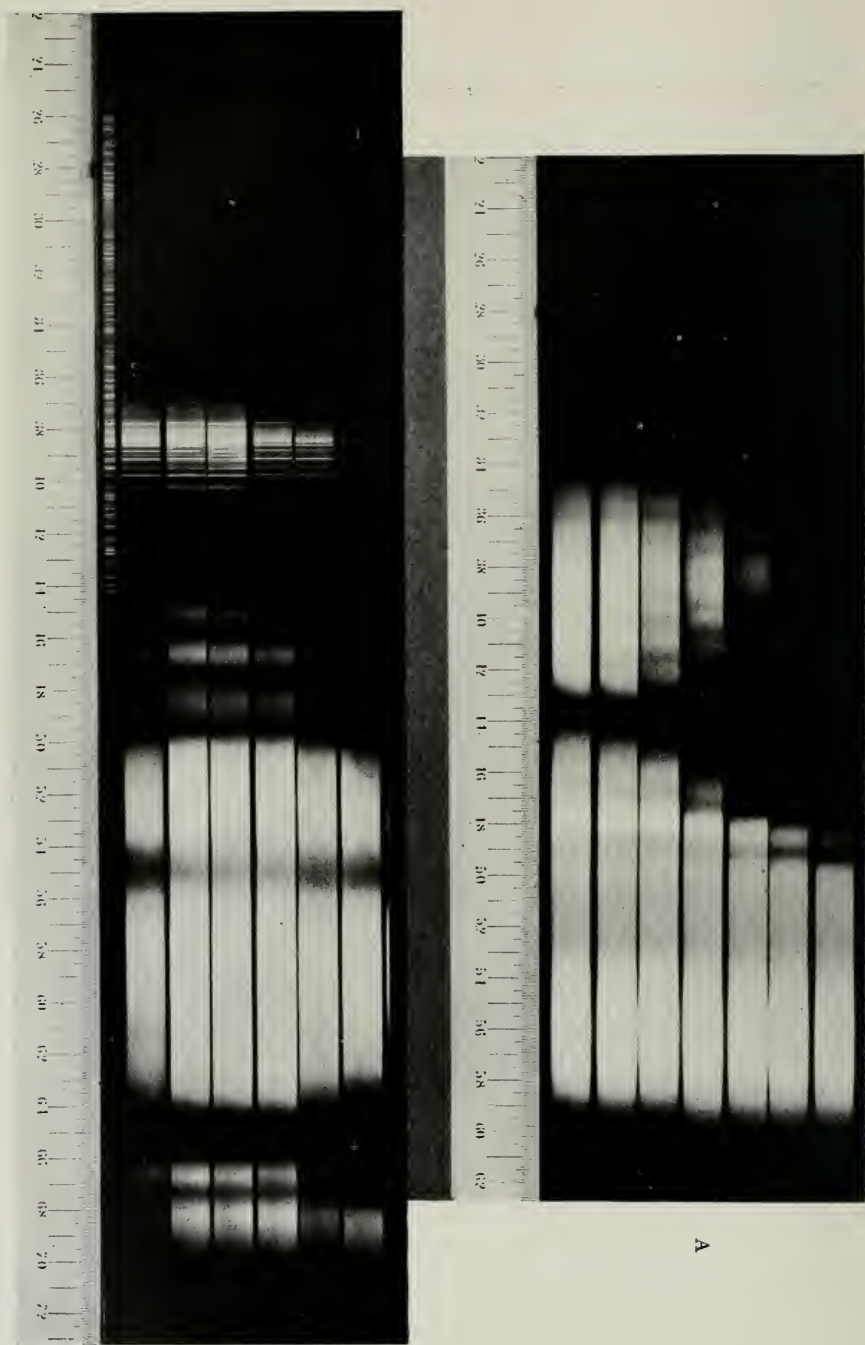
Plate III.
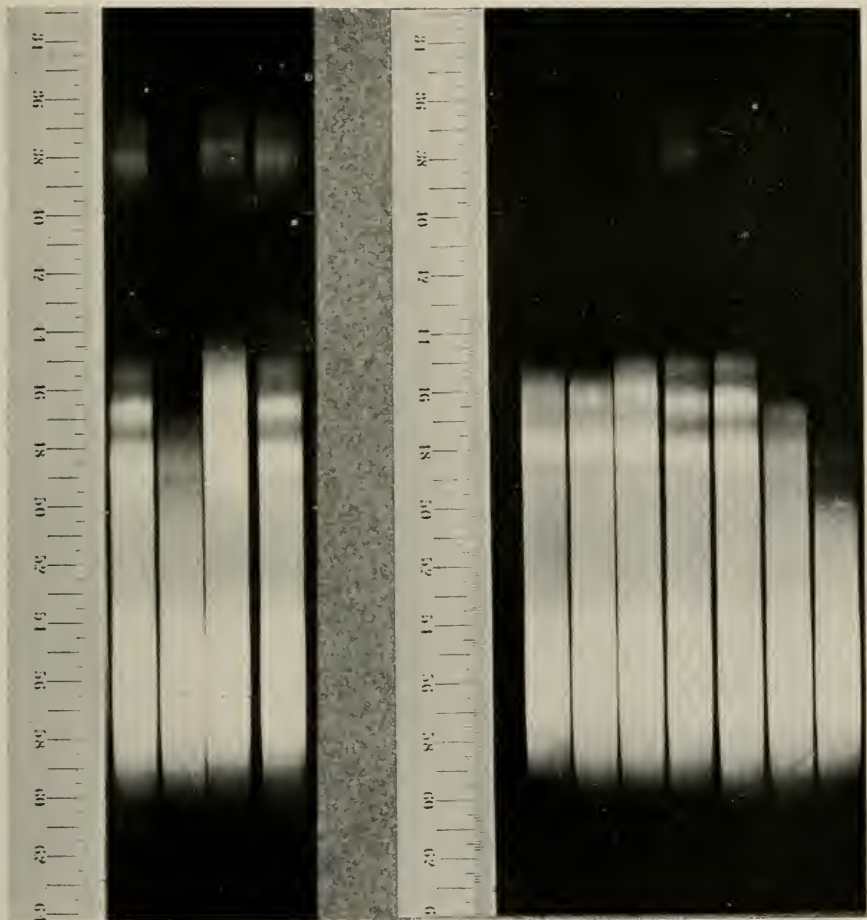
Plate IV.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
λ	4930	4760	4610	4455	4325	4190	4070	3965	3855

(e) *Uranyl Nitrate in Mixtures of Methyl Alcohol and Water.* —In the previous work of Jones and Anderson[1] it was found that in some cases (for example neodymium chloride) a salt in water has a different set of absorption bands as compared with the same salt in another solvent as, *e. g.*, methyl alcohol.

When the salt is dissolved in mixtures of these two solvents, say methyl alcohol and water, it was found that as the amount of one solvent, methyl alcohol for instance, decreased the methyl alcohol bands of the salt decreased in intensity, but did not change their position in the spectrum. At the same time the water bands of the salt became more intense. In the present work it is shown that the uranyl nitrate bands in pure water and in pure methyl alcohol occupy different positions. The problem to be investigated is to find out whether in mixtures of water and methyl alcohol the uranyl bands will show a gradual shift, or whether the methyl alcohol uranyl bands and the water bands will both exist together, their relative intensities being proportional to the relative amounts of methyl alcohol and water. It was found that the two sets of bands exist together and that the methyl alcohol bands decrease in intensity quite rapidly with increase of water. The blue-violet band showed marked changes until the amount of water reached about 20 per cent. In this work the amount of uranyl nitrate in the path of the light was kept constant, and the only variable was the relative amounts of methyl alcohol and water. The above would indicate that uranyl nitrate in water is "hydrated" and in methyl alcohol it is "alcoholated," and that the effect of "hydration" is much more persistent than that of "alcoholation." It is quite possible that this is due to the number of water molecules producing the hydration being greater than that of methyl alcohol molecules taking part in alcoholation.

(f) *Uranyl Nitrate in Ethyl Alcohol.*—The absorption of uranyl nitrate in ethyl alcohol was mapped and the general

[1] Carnegie Institution of Washington, Publication No. 110.

characteristics were found to be the same as for the water and methyl alcohol solutions. A new band was found at λ 5200 which was about 50 A. U. wide. All the uranyl bands were very faint and wide and therefore difficult to measure. There were deviations from Beer's law similar to those found for the methyl alcohol solution. On account of the diffuseness of the bands no spectrograms were made of mixtures of water and ethyl alcohol. Following are approximately the positions of a few of the bands:

	a.	b.	c.	d.	e.	f.	g.	h.	i.
λ	5000	4800	4630	4475	4325	4180	4080	3970	3875

(g) *Absorption Spectrum of Anhydrous Uranyl Nitrate.*— When it was first discovered that the uranyl nitrate "water" bands were all shifted to the violet with reference to the bands of the other uranyl salts in water, as well as with reference to the uranyl nitrate bands in other solvents, it was thought that possibly it was more hydrated than the other salts in solution. The uranyl salts crystallized from water solutions at ordinary temperatures have the following composition: $UO_2(NO_3)_2.6H_2O$, $UO_2SO_4.3H_2O$, $UO_2(CH_3COO)_2.2H_2O$, and $UO_2Cl_2.H_2O$. This fact would favor the supposition that in solution the nitrate might be more hydrated than the other salts. The fact that the absorption of the aqueous solution of the nitrate and the crystallized salt was very much the same, as far as the positions of the uranyl bands is concerned, also seemed to favor this view.

In this connection it was considered important to examine the absorption spectrum of the anhydrous uranyl nitrate. This salt was powdered and placed in a closed glass tube just above the slit of the spectroscope. The light of a Nernst glower was then focused upon the surface of the salt nearest the slit and an exposure of about three hours made. In this way we examine light that has penetrated a short distance into the powder and is then diffusely reflected.

The absorption spectrum was found to consist of quite a large number of bands which seem quite different in many respects from those of the solution. The following are the ap-

proximate wave lengths: $\lambda\lambda$ 4800, 4650, 4500, 4420, 4360, 4280, 4180 (broad), 4060 (broad), 3950 (broad), 3820 (broad), 3700 (narrow) and 3600 (narrow). The bands marked broad are from 50 to 60 A. U. wide and the narrow bands about 20 A. U. If the first band is the a band, then the bands of the anhydrous salt are to the violet of the corresponding bands of the crystals and of the solution. If it is the b band the opposite is the case. On account of the smallness of the intensity of the bands it could not be settled whether λ 4800 is the a or the b band. Further investigation of this point will be made.

There are two difficulties in the above theory, difficulties for which no explanation has thus far been suggested. In the work on the effect of rise of temperature on the absorption spectrum it was found that the uranyl nitrate bands did not shift to the red. On the other hand, the uranyl sulphate and uranyl chloride bands were shifted to the red under the same conditions. (In these cases aqueous solutions were investigated.) If the uranyl nitrate bands owe their position to a large amount of hydration it would be expected that with rise in temperature they would be shifted towards the red more than the bands of the sulphate and chloride. Another difficulty is that of the effect of dilution. The greater the dilution the greater the dissociation, and, therefore, according to the theory of Arrhenius, for very dilute solutions the UO_2 group should exist in the ionic condition and the absorption spectrum of all the salts should be the same, *i. e.*, the uranyl bands should then occupy the same positions independently of the kind of salt. No effect of this kind is to be noticed, as was shown above under the division describing the effect of dilution. It is intended to use much more dilute solutions in the future.

VI. *Absorption Spectra of Uranyl Bromide, Sulphate and Acetate.*

(a) *Uranyl Bromide in Water.*—In B, Plate V, we have the absorption spectra of uranyl bromide (crystalline salt, $UO_2Br_2.H_2O$). The exposures were 1 minute to the Nernst glower

with 0.8 ampere and a slit width of 0.08 mm., and a 3-minute exposure to the spark. The depth of the cell was 3 mm. and the concentrations were 1, 0.75, 0.5, 0.33, 0.25, 0.2 and 0.16 normal, the spectrum for the most concentrated solution being that next to the comparison scale.

It will be seen that uranyl bromide gives rise to an absorption very similar to uranyl nitrate, there being a blue-violet and an ultraviolet band. The absorption for the 1 N solution is complete for all wave lengths less than λ 4470. For 0.75 N the limits of the blue violet band are $\lambda\lambda$ 4450 and 3900, the ultraviolet band beginning at λ 3800. For 0.5 N the blue-violet band shows considerably large transmission, having almost completely faded out. Its middle comes at about λ 4250. The ultraviolet band gradually recedes towards the shorter wave lengths as the dilution increases.

The uranyl bands themselves do not show nearly so prominently as in the case of the chloride and nitrate. The bands are very wide and diffuse. Their approximate positions are:

a.	*b.*	*c.*	*d.*	*e.*	*f.*
4880	4720	4560	4450	4280	4160

The spectrogram showing a series to test Beer's law is given in A, Plate V. The concentrations, beginning with the strip nearest the numbered scale, are 1, 0.75, 0.5 0.33, 0.25, 0.2 and 0.16 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18 and 24 mm., respectively. Beer's law is found to hold, the limits of the absorption bands being independent of the above range of concentrations. The ultraviolet band and blue-violet band have a small region of transmission between them which shows in the original film but not on the print from it. This region of transmission is very faint and is quite a sensitive index to any possible deviations from Beer's law. It shows no changes in intensity with change in concentration. The uranyl bands *a* and *b* show although they are very indefinite. Concentration does not affect their intensity in the least as far as can be detected.

(b) *Absorption Spectrum of Uranyl Sulphate.*—The mapping

Plate V.

B

A
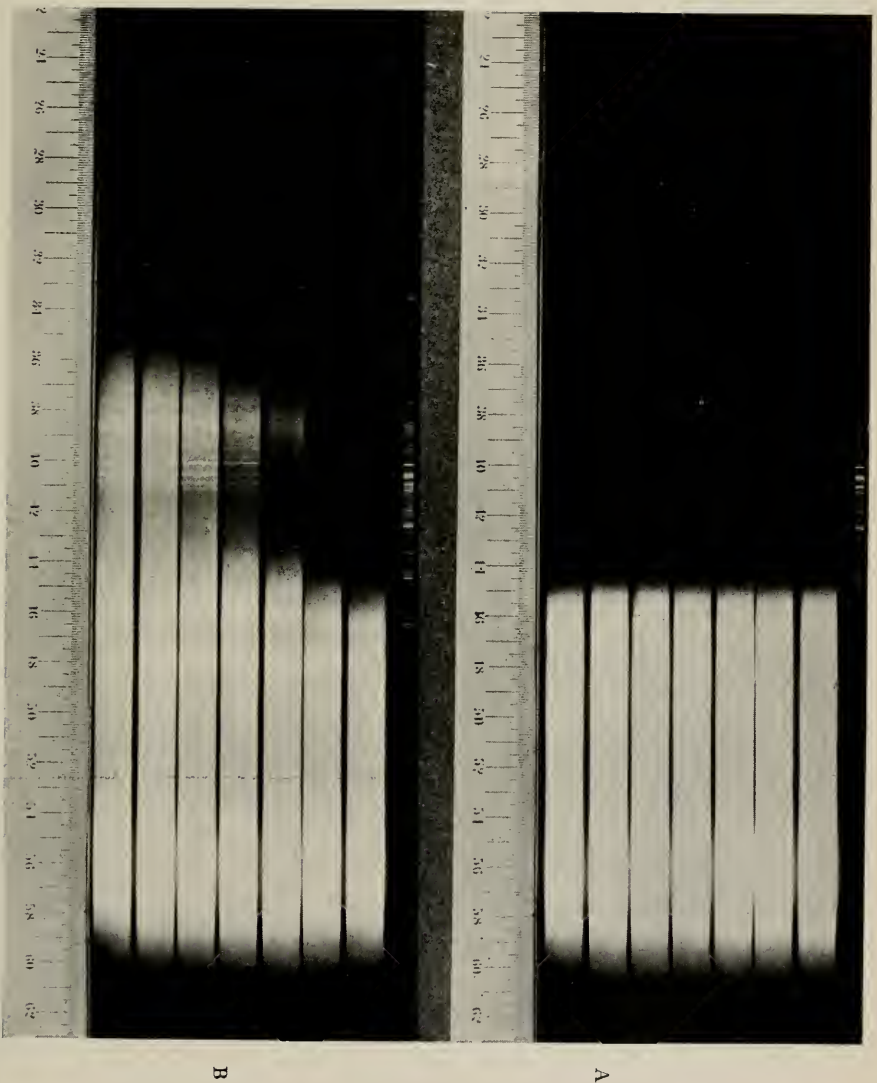
of the absorption spectrum of uranyl sulphate in water showed that it was very much like that of the nitrate in water. As in the case of the nitrate the i band was much weaker than the adjacent bands. Beer's law was found to hold. The addition of a large amount of sulphuric acid was found to make the uranyl bands much sharper, but not to cause them to shift. Much more work will be done on the effect of strong acids on the uranyl bands. The following gives the wave lengths of the sulphate bands:

a.	b.	c.	d.	e.	f.	g.	h.	i.	j.	k.	l.
4900	4740	4580	4460	4330	4200	4070	3970	3850	3740	3630	3530

(c) *Uranyl Acetate in Water.*—Uranyl acetate crystallizes from a water solution at ordinary temperatures as

$$UO_2(CH_3COO)_2 2H_2O.$$

The aqueous solution of this salt is very similar to that of the uranyl salts previously described, showing the blue-violet and ultraviolet bands and also the characteristic uranyl bands. This salt in solution is much more highly colored for the same concentration than the nitrate or bromide.

Plate VI, B, represents the absorption of a series of solutions where the concentration was kept constant and the depth of layer varied. The usual procedure was to keep the concentration constant and vary the depth of cell. For salts obeying Beer's law, this would give the same absorption as keeping the depth of cell constant and varying the concentration so that in our spectrograms of a salt where Beer's law holds, no difference is made between these two cases. Where Beer's law is deviated from, the two cases will not be identical. For the case under consideration the concentration was 0.031 N and the depths of cell, starting with the strip nearest the numbered scale, were 24, 18, 12, 9, 6, 4 and 3 mm. The length of exposure to the Nernst glower with 0.08 ampere and a slit width of 0.08 mm. was 1 minute.

The blue-violet band has the boundaries $\lambda\lambda$ 4500 and 4050 for a 24 mm. cell, and $\lambda\lambda$ 4400 and 4100 for a depth of 18 mm., the middle of the band thus coming at about λ 4250. The

long wave length edges of the ultraviolet band are $\lambda\lambda$ 3750, 3700, 3680, 3660, 3630, 3600 and 3580 for depths of cell of 24, 18, 12, 9, 6, 4 and 3 mm., respectively.

A photograph was made to bring out the small uranyl bands. An exposure was first made for 1 minute (0.08 ampere and 0.08 mm. slit) in the yellow end of the spectrum. This solution was 15 mm. deep in every case. The screen was interposed so as to cut off all light of greater wave length than λ 4450. A long exposure to the Nernst filament—about 5 minutes—was then made. Another screen was then interposed which cut out all light of wave length greater than λ 2800, and an exposure made to the spark. During these three exposures nothing was moved except the screen and thus the question of any mechanical moving of the photographic film was eliminated. From these two plates the positions of 9 uranyl bands were measured. These were as follows:

a.	b.	c.	d.	e.	f.	g.	h.	i.
4910(?)	4740	4595	4455(?)	4310	4160	4070	3970	3865

It will be seen that these bands are all nearer the red than the bands of uranyl nitrate in water.

Deussen found the following values:

a.	b.	c.	d.	e.	f.	g.	h.	i.	j.
4875	4730	4575	4420	4310	4180	4060	3950	3860	3770

These are in quite good agreement with the values given above.

The spectrogram A, Plate VI, represents change in absorption of uranyl acetate with concentration when the amount of salt in the path of the light beam is kept constant. The exposure was 1 minute to the Nernst glower, with 0.8 ampere (slit 0.08 mm.), and 3 minutes to the spark. Starting from the comparison spectra the concentrations are 0.25, 0.185, 0.125, 0.083, 0.0625, 0.042 and 0.031 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18 and 24 mm.

This uranyl salt shows a deviation from Beer's law which is different from the deviation of any salt previously studied.

Plate VI.
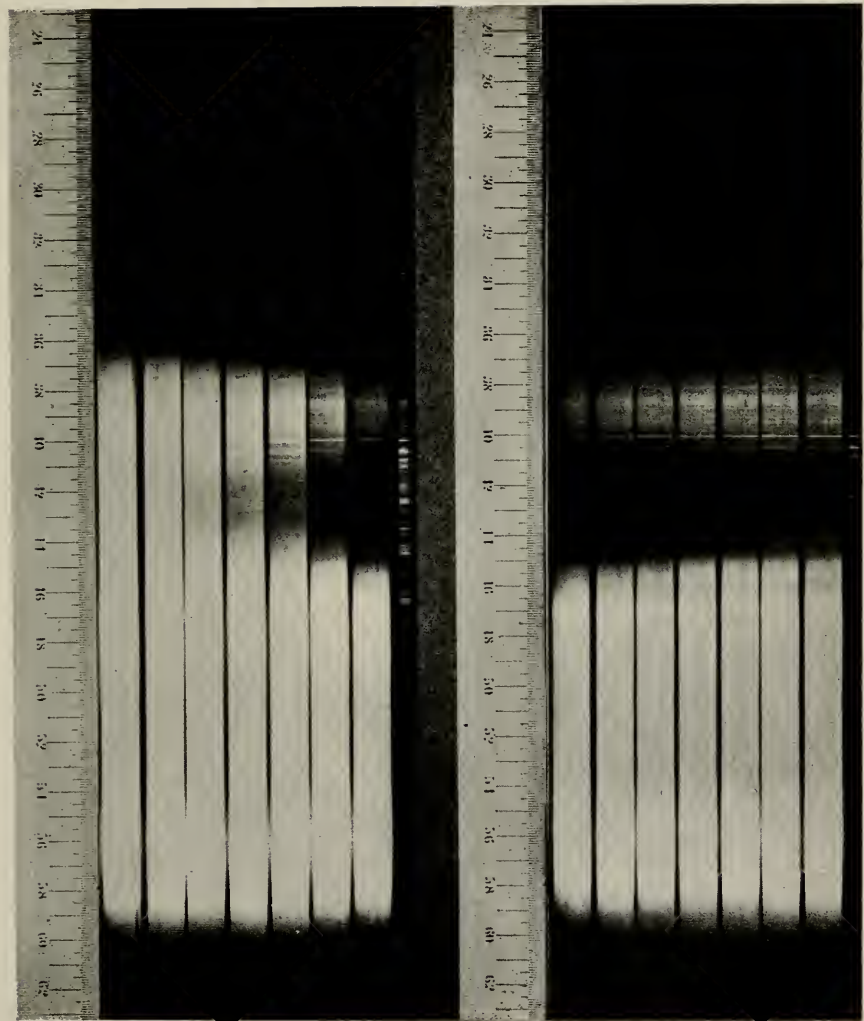
B

A

All other salts show, for a Beer's law series, a greater absorption at the greater concentration. Uranyl acetate shows the opposite, a greater absorption for the less concentrated solutions. For the 0.25 N solution the blue-violet band extends from λ 4150 to λ 4250. At 0.031 N it has broadened, so that its limits are $\lambda\lambda$ 4500 and 4050. This broadening of the absorption is gradual. In like manner the ultraviolet band extends to λ 4400 for the 0.25 N solution and to λ 4300 for the 0.031 N solution.

A 0.188 N solution of uranyl acetate 14 mm. in length was diluted to 0.007 N and 380 mm. in length. The absorption was found to be greater for the more dilute solution. The uranyl bands were not shifted and were much broader in the dilute solution.

(d) *Anhydrous Uranyl Acetate.*—To determine whether the water of crystallization of uranyl acetate, $UO_2(CH_3COO)_2 \cdot 2H_2O$, had any effect on the position of the uranyl acetate bands, the absorption of the anhydrous salt was found in the same way as for uranyl nitrate. Seven bands could be detected, but most of them were quite faint, although stronger than the bands of the nitrate:

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
4905	4775	4605	4460	4320	4200	4085

It will be seen that there is a slight shift towards the red as compared with the aqueous solution.

(e) *Uranyl Acetate in Methyl Alcohol.*—For the uranyl acetate the exposure to the Nernst glower, with 0.8 ampere and a slit width of 0.08 mm., was 1 minute. No exposure was made to the spark except for a comparison spectrum. Starting with the strip nearest the scale, the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07 and 0.06 N. The depth of cell was constant, 6 mm. The edges of the blue-violet absorption were as follows: 0.25 N, $\lambda\lambda$ 4550 and 3850, 0.20 N $\lambda\lambda$ 4520 and 3900, 0.16 N $\lambda\lambda$ 4500 and 3950, and 0.12 N $\lambda\lambda$ 4550 and 4000. The middle of the band would thus come

at about $\lambda\,4270$. As the spark was not used the exact edges of the ultraviolet band cannot be given.

The uranyl bands had the following positions:

a.	b.	c.	d.	e.	f.	g.	h.
4875	4720	4585	4445	4320	4185	4070	3975

A plate was made to test Beer's law. Starting with the strip nearest the comparison scale the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07 and 0.06 N, the corresponding depths of cell being 6, 7.5, 9.5, 12, 15, 19 and 24 mm. The deviation from Beer's law is the same in direction as for uranyl acetate in water solution and is not nearly so great. For the 0.25 N solution the limits of the blue-violet band were $\lambda\lambda$ 4470 and 3925, the distance between the blue-violet band and the ultraviolet band at this concentration being about 100 A. U. units. For the 0.06 N solution the blue-violet and ultraviolet bands have completely merged and the limit of absorption is about $\lambda\,4600$.

(*f*) *The Uranyl Bands of the Acetate.*—The following table gives the approximate wave lengths of the uranyl bands of the acetate in water and in methyl alcohol, and of the anhydrous powder.

Bands of Uranyl Acetate.

	a.	b.	c.	d.	e.
Water	4910	4740	4595	4455	4310
Methyl alcohol	4900	4770	4600	4460	4320
Anhydrous salt	4910	4760	4610	4460	4330

	f.	g.	h.	i.
Water	4160	4070	3970	3830
Methyl alcohol	4200	4090	....	....
Anhydrous salt	4190	4070	3980	....

From this table it seems that the positions of the bands of the acetate under these different conditions are about the same.

VII. The Phosphorescent and Fluorescent Spectra of Uranium.

Many bodies on being exposed to light, X-rays, α, β, γ or cathode rays, on being heated or rubbed, emit light. This is

generally called phosphorescence when the light is emitted after the stimulating agent ceases to act, and fluorescence when the excited light ceases to be emitted as soon as the exciting cause ceases. In general, liquids and gases fluoresce while solids phosphoresce. Some of the strongest phosphorescent compounds are the uranyl salts. These salts emit bands of phosphorescent light in the green region of the spectrum.

A considerable amount of work on the phosphorescence of uranyl compounds has been done by the Becquerels. E. Becquerel[1] found that the phosphorescent spectra of pure uranyl chloride and of double salts of uranyl and potassium or ammonium were quite different, and that apparently the presence of potassium and ammonium caused the bands to shift towards the longer wave lengths. The wave lengths of the bands as given by Becquerel are:

Phosphorescent Bands.

	1.	2.	3.	4.
Uranyl nitrate	6544	6180	5810 / 5860	5590
Uranyl acetate	6525	6180	5860	5590
Uranyl chloride	....	6230	5955	5685
Uranyl sulphate	6620	6262	5955	5690

	5.	6.	7.
Uranyl nitrate	5325 / 5325	5090	4920
Uranyl acetate	5325	5090	4920
Uranyl chloride	5433	5176	4980
Uranyl sulphate	5418	5170	4945

The bands of the nitrate and acetate come at about the same place in the spectrum, whereas the chloride and sulphate bands are farther towards the red. H. Becquerel[2] finds that at low temperatures the phosphorescent uranyl bands become quite sharp in the same way that absorption bands do. For uranyl nitrate he gives the following table:

[1] Ann. Chim. Phys., [4] **27**, 539–579 (1872).
[2] Compt. Rend., **144**, 459–462 (1907).

Phosphorescent Spectrum of Uranyl Nitrate.

Room temp.	Liquid air temp.	Room temp.	Liquid air temp.
6210–6150	6360	5360–5280	5327–5320(s)
	6175–6165		5303–5292(s)
	6145–6127		5272
	6104		5240
	6005–6045		5190
5940–5840	5860–5853(s)		5137
	5837–5830(s)	5120–5060	5115
	5782		5097–5090(s)
	5707		5074–5070(s)
	5630		5018
	5600		4975
5630–5550	5585–5575(s)		4925
	5558–5548(s)	4893–4855	4903–4896(s)
	5490		
	5435		
	5375		

Further work has recently been published by J. Becquerel and Onnes.[1] At the temperature of solid hydrogen the intensity of emission is not diminished and the bands which existed at liquid air temperatures undergo further subdivision. Lowering the temperature shifts the emission bands towards the violet. For instance, for the double sulphate of uranyl and potassium:

80° K	4904.2	5114.8	5342.4	5590.9	5863.1
20° K	4903.4	5113.5	5341.0	5588.9	5860.5
	0.8	1.3	1.4	2.0	2.6

The displacement of the phosphorescent bands caused by lowering the temperature from 20° to 14° is very small, and it is quite possible that as the temperature is lowered the bands approach asymptotically a limiting position. Becquerel and Onnes find that the difference in the appearance of the different groups of bands is the result of successive ascending changes in the relative intensities of the bands in these groups. They find, when crystals of double salts are used, that the spectrum depends more upon the acid of the salt than upon the other base. The differences between the frequencies of two suc-

[1] Commun. Phys. Lab., Univ. Leiden, Nos. 110, 111.

cessive homologous bands are practically constant, not only
for the same, but also for all series of homologous bands of the
same salt. The values of this constant for the various salts
differ but slightly from one another.

At low temperatures the phosphorescent spectrum of uranyl
compounds resembles that of the channeled spectrum of nitro-
gen and carbon. Becquerel and Onnes consider both to have
the same character. Placing the phosphorescing uranyl salt
in a powerful magnetic field did not produce any noticeable
effect upon the uranyl bands. Some of the bands become
arbitrarily absorption or emission bands, and at low tempera-
tures the wave lengths are the same for both kinds of bands.
Following is a table giving the wave lengths of the phosphor-
escent bands of various uranyl salts at 80° C.

The authors have done a little work on the phosphorescent
spectra of uranyl compounds. For the stimulation of the
phosphorescent bands either sunlight or the light from a
spark has been used. The glass screens previously described
or a Feuss monochromatic illuminator were used when only
certain wave lengths of exciting light were needed. In the
case of uranyl nitrate it was found that practically no phos-
phorescence was excited unless the exciting light had a wave
length less than λ 4900. For all wave lengths less than this,
phosphorescence was excited, but the bands seemed the same,
irrespective of the wave length of the exciting light. It seems
that the energy that is absorbed by the series of uranyl absorp-
tion bands is partly radiated as the energy of the phosphor-
escent bands. This suggests a number of lines of work which
we hope to carry out in the future. Among these are the
following: Are the phosphorescent bands of the salts of
uranyl affected in the same way as the uranyl absorption
bands? In the case of uranyl chloride can phosphorescent
light be excited by the bands in the region λ 6000? Does
light of wave lengths between that of the uranyl absorption
bands excite phosphorescence? In the case of uranyl nitrate
obtained from an alcoholic solution would light of wave length
greater than λ 4900 excite phosphorescence?

Jones and Strong.

Phosphorescent Bands.

Double sulphate of uranyl and sodium.	4891.5	5101.2	5330.0	5578.5	5881.1	6184.0
	....	5125.4	5354.7	5604.6	5908.0	6215.7
Double sulphate of uranyl and ammonium.	4912.6	5124.5	5355.4	5607.4	5910.1	6219.5
	4934.7	5147.8	5380.1	5633.3	5938.8	....
Uranyl sulphate.	4918.3	5133.9	5369.4	5626.8		
	....	5160.2	5395.8	5654.0	5832.9	
Uranyl nitrate.		5069.6	5301.5	5554.6		
Double acetate of uranyl and sodium.	4732.5					
	4762.3	4932.5	5148.6	5384.5	5642.7	
	4769.2	4950.2	5167.8	5404.5	5663.4	
	4785.8	4964.9	5184.9	5424.0	5685.8	
	4794.6	4972.1	5192.2	5431.6	5694.6	
		4990.2	5221.4	5463.5		
		4999.2				

Different salts of uranyl phosphoresce very differently. The specimens of uranyl chloride gave very weak and diffuse bands. Uranyl nitrate obtained from the evaporation of a methyl alcohol solution showed no phosphorescence. Uranyl bromide also gave very little phosphorescent light on excitation. Using the Hilger spectroscope, the following approximate wave lengths for bands of various salts were found:

Uranyl sulphate	5660	5580	5420	5315
Uranyl nitrate	5670	5600	5410	5330
Uranyl acetate	....	5570	....	5340
Uranyl sulphate	5210–5160	5085	4950	4860
Uranyl nitrate	5180	5100	4970	4840
Uranyl acetate	....	5070	....	....

The bands are so hazy and wide that these measurements mean very little.

Very little has been done on the fluorescence of solutions of uranyl salts. Some work by Stokes,[1] Becquerel,[2] Morton and Bolton,[3] and others, treats of fluorescent bands. Morton and Bolton give the following wave lengths for some of the fluorescent bands of the solid salts:

Uranyl acetate, solid	6240	6070	5760	5500
" chloride, solid	6300	6000	5660	5400
" monophosphate, solid	6510	6170	5850	5600
" " in solution	6470	6200	5910	5650
" sulphate	6520	6150	5870	5600
" " anhydrous	6580	6230	5930	5630
Uranyl acetate, solid	5240	5030	....	....
" chloride, solid	5180	4930	....	....
" monophosphate, solid	5200	5100	4880	4720
" " in solution	5380	5160	4920	4800
" sulphate	5340	5110	4890	4770
" " anhydrous	5365	5145	4850	4780

VIII. The Absorption Spectra of Solutions of Uranous Salts.

Very little work has been done up to the present on the absorption spectra of uranous salts, largely because of their

[1] Phil. Trans., **1852**, II, 463; **1853**, III, 385.
[2] Ann. Chim. Phys., [3] **55**, 86 (1859); [3] **57**, 101 (1859); [4] **27**, 639 (1872).
[3] Chem. News, **28**, 47, 113, 164, 233, 244, 257, 266 (1874).

very unstable character in solution. J. Formánek[1] describes the absorption spectra of uranous chloride. This was prepared by adding a little zinc and hydrochloric acid to a uranyl chloride solution. He found that the spectrum changed as the uranyl chloride was being reduced. A very strong band was found at λ 6507. The other bands, eleven in number, were $\lambda\lambda$ 6722, 6367, 6165, 6030, 5782, 5497, 5238, 5064, 4962, 4840 and 4519.

A similar method has been used by the writers. The uranous nitrate, sulphate and chloride were formed by adding the corresponding acid to a solution of the uranyl salt containing some zinc. The uranous chloride and sulphate were quite stable in solution, remaining reduced for weeks. Uranous sulphate crystallizes out from solution as $U(SO_4)_2.9H_2O$. Solutions in alcohol can be reduced just as easily as solutions in water. Uranous nitrate was found to be very unstable. At the present writing a number of spectrograms have been made, and much more work will be done on these uranous salts and on the absorption spectra of the various oxides. It has already been found that uranous chloride has very different spectra in different solvents.

Uranous Sulphate.—Plate VII, A.—Only one spectrogram has as yet been made with uranous sulphate,

$$U(SO_4)_2.9H_2O,$$
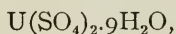
in water. The bands are quite similar to the uranous chloride bands. The absorption in the blue and shorter wave lengths is complete. The following bands appeared: $\lambda\lambda$ 6700, 6500, 6300, 5480 and 4900. The 6500 band was the strongest of all and on increasing the depth of cell this widened out and, uniting with the 6700 and 6300 bands, formed one very wide absorption band extending over hundreds of Angström units. The 6300 band is very weak, the 6700 band somewhat stronger. The 5480 band is somewhat weaker than the 4900 band. On increasing the depth of cell these two bands widen enormously.

From a comparison of uranous chloride and uranous sul-

[1] Die qualitative Spektralanalyse, p. 99.

Plate VII.

B

A
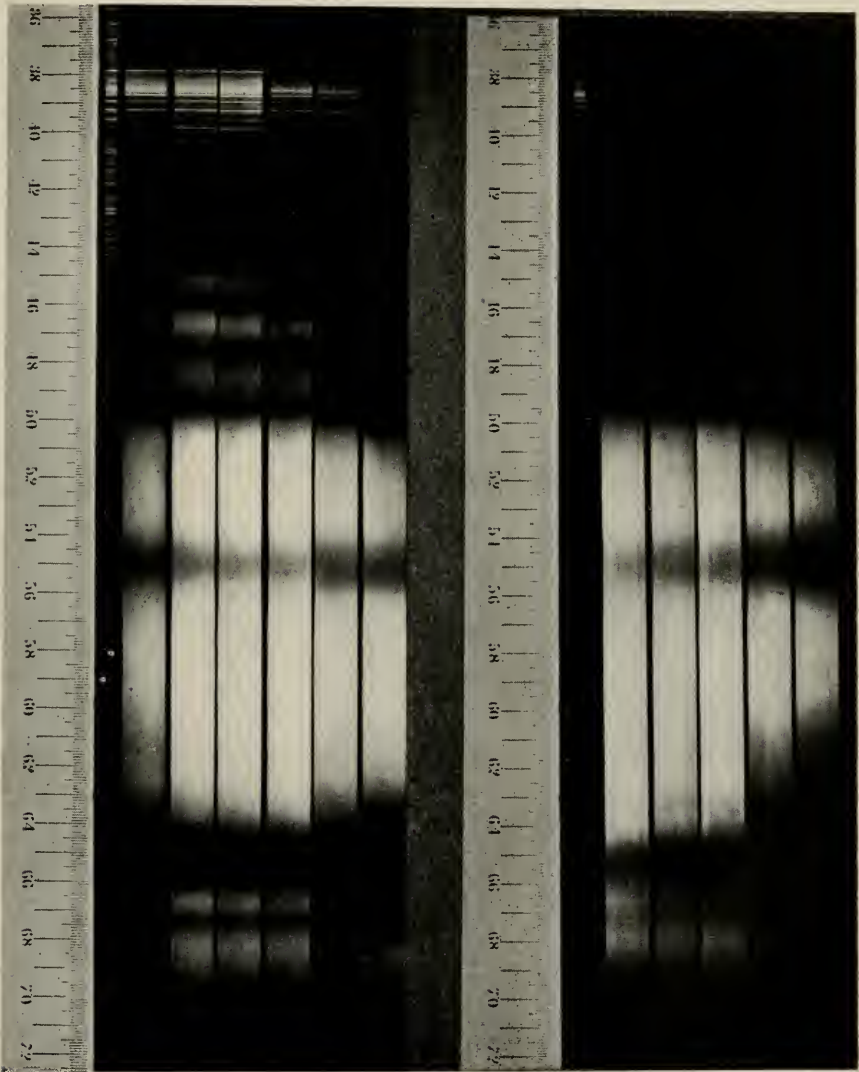
phate absorption spectra, it is seen that the relative intensities and positions of the bands for the two salts are the same.

A uranous chloride solution, Plate VII, B, was made by adding hydrochloric acid and metallic zinc to a normal uranyl chloride solution. In a short time the solution became very green in color and gave the characteristic uranous spectrum. Besides the bands above described for the sulphate there appeared three very strong bands in the blue-violet region, $\lambda\lambda$ 4600, 4770 and 4970. The other bands, $\lambda\lambda$ 5520, 6350, 6530 and 6750, were the same as for uranous sulphate previously described.

To a 0.25 normal solution of uranyl chloride in methyl alcohol was added a small amount of hydrochloric acid and zinc. This reduced the yellow uranyl chloride to the green uranous chloride. The absorption spectrum, Plate VIII, B, of uranous chloride in methyl alcohol was found to be different from that of the same salt in water. Bands closely resembling the bands in water appeared at $\lambda\lambda$ 4600 and 4780. The water band, λ 4970, was broken into two bands in methyl alcohol, $\lambda\lambda$ 4930 and 5030. In the alcohol there was a very broad weak band at about λ 5300. This did not appear at all in aqueous solution. The band at λ 5580 is quite like the water band. Weak and broad alcohol bands appear at $\lambda\lambda$ 6150, 6300, 6480. A strong band appears at λ 6750. As the depth of the alcoholic solution is increased the widening of the bands is quite unlike the widening of the water bands with increased depth of layer.

In this plate (B, Plate VIII) the three lower strips represent the absorption spectra of uranous chloride in methyl alcohol, and the upper strip is made to show the difference between this and the absorption of a solution of uranous chloride in water.

A, Plate VIII, represents the absorption of uranous chloride in water, the depth of cell being varied.

The alcohol bands $\lambda\lambda$ 4600 and 4780 and 5580 are slightly shifted towards the red with reference to the analogous water bands.

To a solution of uranyl chloride and calcium chloride in water some hydrochloric acid and a little metallic zinc were added. The absorption spectrum of this solution was very similar to that of the water solution of uranous chloride except in the blue and violet part of the spectrum. In this region there was an almost general transmission. A broad diffuse band appeared at λ 4300, and a very weak band at λ 4600. The other bands had about the same relative intensity and position as the pure water bands.

IX. *The Various Uranium Spectra.*

Plate III, B, was made under the usual conditions of slit width and integral intensity of the penetrating light beam. Starting with the strip next the numbered scale, the absorption spectrum is that of (1) a normal aqueous solution of uranyl sulphate 3 mm. thick; (2) a 0.25 normal aqueous solution of uranyl acetate 12 mm. thick; (3) a 0.75 normal aqueous solution of uranyl nitrate with 3 mm. depth of cell; and (4) 0.75 normal aqueous solution of uranyl sulphate, 4 mm. thick. The plate shows the greater relative absorbing power of uranyl acetate, the broadness of the uranyl bands of the acetate and also the fact that the uranyl bands of the nitrate are further towards the violet than the corresponding bands of the other salts.

Collecting the data for the various salts in different solutions we have the following:

Plate VIII.
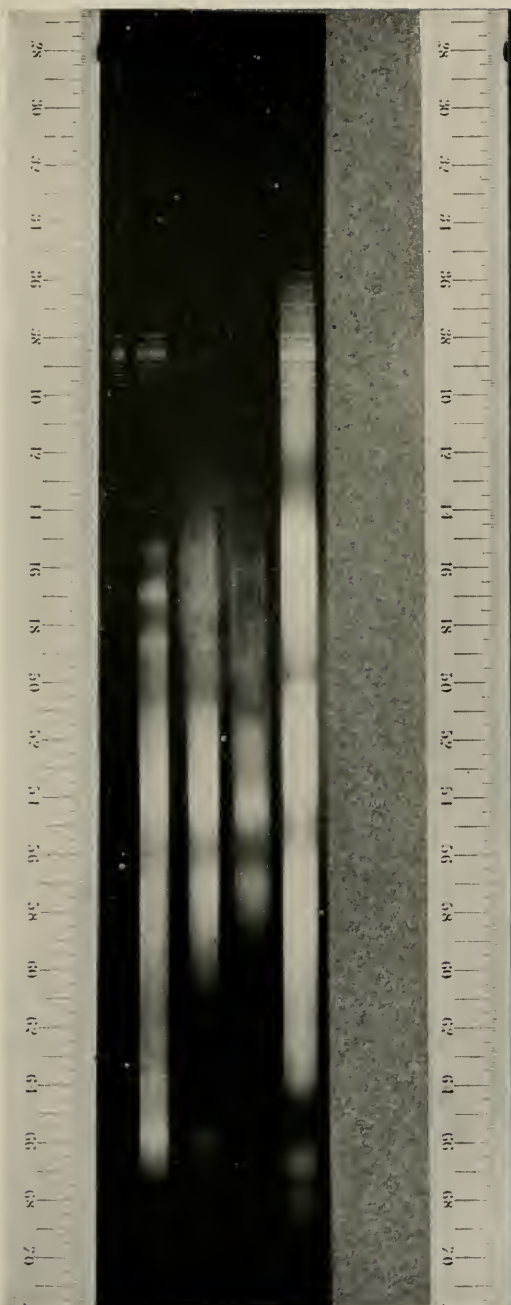
Uranyl Bands.

	a.	b.	c.	d.	e.	f.	g.	h.	i.	j.	k.
Chloride in water	4920	4740	4560	4460	4415	4170	4025	....	....	....	....
Chloride in methyl alcohol											
Chloride in ethyl alcohol	4930	4760	4610	4465	4345	4220	4090	3980	3860	3760	
Chloride and calcium chloride in methyl alcohol	4900	4750	4580	4400	....	4250	4100	3980	3860		
Bromide in water	4880	4720	4560	4450	4280	4160	4010	....	....	....	....
Sulphate in water	4900	4740	4580	4460	4330	4200	4070	3970	3850	3740	3530
Nitrate in water.	{4890 / 4800}	{4742 / 4722}	4540	4390	....	4155	4030	3905	3815	3710	3515
Nitrate in methyl alcohol	4930	4760	4610	4460	4325	4190	4070	3970	3855	....	....
Nitrate in ethyl alcohol	5000	4800	4630	4475	4325	4180	4080	3970	3875	....	....
Acetate in water	4910	4740	4595	4455	4310	4160	4070	3970	3865	....	....
Acetate in methyl alcohol	4900	4770	4600	4460	4320	4200	4090	3975	....	....	....

Bands of Some Uranous Salts.

	a.	b.	c.	d.	e.	f.	g.	h.	i.	j.	k.
Uranous and aluminium chlorides in water	6730	6730	6530	6530		{6300 / 6150 / 6080 / 5900}	5510			
Uranous and calcium chlorides in water	6740	6740	6520	6520		5900	5500		4950	{4720 / 4570}
Uranous chloride in methyl alcohol	6750	6750	6480	6480		{5570, 5300}				
Uranous chloride in ethyl alcohol	6790	6790	6535	6535		6340	5610		4920	
Uranous nitrate in water	6700	6700	6470	6470		5900	....		....	
Uranous sulphate in water	6730	6730	6550	6550		....	5500		....	

It is a fact that investigations on the spectral emission and absorption of bodies have been far less fruitful in extending our knowledge of the structure of the atom than had been expected. This is largely owing to the almost infinite complexity of the structure of the atom and our general ignorance of the forces that exist there. Probably the best known example is that of the uranyl group which we have been describing. Let us consider the spectral vibrations that can be produced by components that exist or may be produced from the apparently simple UO_2 group: (1) We have the absorption spectrum described above. At low temperatures most of these bands break up into much finer bands. (2) The uranyl salts under various methods of excitation emit a phosphorescent spectrum of a large number of rather fine bands throughout the visible region of the spectrum. It is quite possible that this spectrum is intimately connected with that of the absorption spectrum. (3) We have the absorption spectrum of the uranous salts which has been described above. This spectrum has been probably caused by the change of valency of the uranium atom. Uranium is known to form quite a large number of oxides and it is quite possible that for each valency of the uranium we have a characteristic spectrum. (This also is being investigated.) It is also quite probable that at lower temperatures those spectra would consist of quite fine bands. (4) We have the spark spectrum and the absorption spectrum of oxygen, and (5) that of ozone which bears no relation to that of oxygen. (6) There is the exceedingly complex spark spectrum of uranium consisting of thousands of fine lines and also (7) the complex arc spectra. From radioactive experiments it is known that uranium is continually breaking down into ionium. (8) Ionium possesses the properties of a chemical atom and most likely has a spectrum of its own. This would make eight spectra. (9) Ionium breaks down into the radium and radium has a very characteristic spark spectrum, as does also (10) the radium emanation. During the various radioactive transformations several α-particles are emitted with a velocity almost as great as that of light. It is probable that these particles are mov-

ing with very great velocities in the uranium atom under ordinary conditions. (11) The α-particles are known to be charged helium atoms and therefore under proper excitation would give the helium spectrum. The radium emanation breaks down into radium A, B, C, D, E and F. These products behave like chemical elements and probably have characteristic spectra. (12) The final product is lead, which has very complex spark and arc spectra. During these transformations several electrons have been thrown off from the various products with enormous velocities. In a very large number of the above spectrum lines the Zeeman effect indicates the presence of negative electrons and charged doublets.

We thus see what an extremely complex system the group UO_2 must be, and it might seem almost hopeless to disentangle the mystery of its various spectra. At present we know that the arc and spark spectra problem is very complex and that we have very few methods of producing any changes in them. Practically the only method of changing the frequency of these vibrations is by applying a very powerful magnetic field or great pressure and these changes in the frequency are very small. One very important result, however, has been obtained by Kayser, Runge, Wood and others. This work consists in separating spectrum lines into various series. A series of lines are those whose intensity and Zeeman effect vary in the same way when the conditions outside the atom are changed. The work of Wood is important as showing that spectrum lines are due to different systems of vibrators inside the atom. By using monochromatic light of different wave lengths he has been able to excite different series of lines which constitute altogether the fluorescent spectrum of the element.

Present theories of the atom usually regard the electrons and other vibrators that are the sources of arc and spark lines as being well within the atom and as affected by external physical conditions only under very special circumstances. Stark believes that these electrons may rotate in circular orbits, the locus of the centers of these orbits being a closed curve, say a circle. This system will be equivalent to a positive or negative charge according to the sense of rotation of

these electrons. These electrons we will call ring electrons. Supposing these systems to be positive charges, it will require electrons to neutralize these charges. Several of these neutralizing electrons may be in the outer parts of the atom and under certain conditions might be knocked off from the atom. These easily removable electrons will be called "valency" electrons, and can exist under different conditions of "looseness" of connection with the atom. Most of the neutralizing electrons will probably lie far within the atom. For instance, we would expect that in the uranium atom the charged helium atoms are neutralized by negative electrons.

Our theory is that the finer absorption bands of such salts as neodymium, erbium and uranium are due to vibrations of these neutralizing electrons, and that the forces acting upon these are considerably different from those acting on the ring electrons, which, in many cases, give a normal Zeeman effect. It is probable that these neutralizing electrons play the greatest rôle in the optical properties of bodies, such as the properties determining the index of refraction, the extinction coefficient, etc.

Usually the equation of motion of such an electron is given by an equation like the following when a light wave of an electric field $E \cos pt$ is passing by it:

$$m \frac{d^2x}{dt^2} + k \frac{dx}{dt} + n^2x = E \cos pt,$$

where m is the total mass (electromagnetic and material) of the electron, $k \, dx/dt$ is the damping or frictional term and n^2x is the quasi-elastic force. It is an experimental fact as shown by the above work and the work of other investigators, that k and n^2 are not only functions of the electron and the atom, but that they are also functions of the physical and chemical conditions existing in the neighborhood of the atom.

On the other hand, the effect on k and n^2 for a ring electron, when external physical and chemical conditions are changed, is very small. It is for this reason, and the probable fact that there are relatively few neutralizing electrons, that we

believe that much greater progress can be made in determining some of the properties and constitution of various interatomic systems of atoms and molecules by the study of the absorption spectra of uranium and neodymium than by a study of the arc or spark spectra of the same.

The method of attacking the above problem will be to study the effect on the spectra of a body produced by changing the physical and chemical conditions about the light absorbers or emitters within as wide ranges as possible. Some of the possible changes that can be made are as follows: Take for instance the uranyl group UO_2. We can find the effect upon the absorption bands produced (1) by diluting the solution, (2) by changing the acid radical to which the uranyl group is united, (3) by changing the solvent and using mixtures of solvents, (4) by adding other salts (like aluminium chloride), or (5) by adding acids of the same kind as that of the salt of the uranyl group. The effect (6) of adding foreign salts and acids at the same time and then varying the solvent, or the temperature, can also be tried. In this way a very large number of very interesting things can be tested. In most of these changes lc will be kept constant.

In the above example the temperature (7), the external pressure (8), the electric field (9) and the magnetic field (10) can be changed between wide limits. The latter effect is a very important one. For example, in aqueous solution neodymium salts give a large number of fine bands, in glycerol there are quite a number of new bands replacing the "water" bands, and in the alcohols there are various "alcohol" bands. At low temperatures these bands become very fine and it is quite possible to detect the Zeeman effect. Now it seems quite probable that a "glycerol" band and an "alcohol" band that seem to replace each other as the solvent is changed are both due to the same vibrator. If the Zeeman effect is the same in both cases it would be a strong argument in favor of the above theory. A case that will soon be described is very important. It was found that the wave lengths of certain neodymium lines in a pure water solution did not change when the temperature was raised from 0° to 90°. If, how-

ever, calcium chloride was added, then on raising the temperature the above bands were shifted to the red. A very interesting and important investigation is whether the Zeeman effect on the band would be affected by the presence of substances like calcium chloride.

To be compared with the above changes are changes in the absorption spectra of the crystals of the salt (11) as affected by water of crystallization, or by the presence of foreign substances, or as affected by the polarization (12) or direction of passage of light through the crystal. The absorption spectra (13) of the anhydrous powder at different temperatures, etc., should be found. The phosphorescent spectrum (14) should be studied in this connection, especially as affected by the mode of stimulation (X-rays, cathode rays, heating or monochromatic light of different wave lengths). The temperature, electric or magnetic field could be changed about the phosphorescing body. The effect of change of state (15) should be tried if this is possible, also any possible changes of valency of the atoms (16) composing the body investigated. We shall attack the problem from all of these standpoints.

After correlating the data obtained by the above named investigations it is pretty certain that it will be possible to take each vibrator and trace the effects produced upon it by the above changes. It is also quite certain that we shall also know something of the nature of the vibrating system and the part that it plays in that complex body we call the atom.

For instance, let us take the bands of uranyl nitrate. It was found that the uranyl bands of an aqueous solution of the nitrate had shorter wave lengths than that of any other uranyl salt in water. The uranyl bands of the nitrate in other solvents were farther towards the red than the bands of an aqueous solution. Now although the solvent has a great effect upon the bands, nevertheless it seems quite certain that the NO_3 group has a very considerable effect upon the vibrations of the uranyl group. If it were possible to find the ratio e/m for the vibrators in this case by the Zeeman effect, it might be possible to find an approximate value for the force exerted by the NO_3 group upon the vibrator. It seems quite

certain that this force differs for the vibrators producing differ-
ent bands. The measurements of the wave lengths of the
uranous bands are as yet very few, yet they seem to indicate
that for aqueous solutions of the uranous salts, the bands of
the nitrate are farther towards the violet than the bands of
the other uranous salts. The values given for the phosphor-
escent bands by E. Becquerel (p. 73) and by J. Becquerel (p.
74) indicate that the bands of the nitrate are further towards
the violet than those of the other uranyl salts. We thus see
that throughout these three spectra the NO_3 group exerts a
similar force upon the vibrators that are the cause of the
bands.

X. *The Absorption of Neodymium Chloride in Glycerol and in Mixtures of Glycerol and Water.*

The absorption spectrum of a glycerol solution of neodym-
ium chloride is much like that of the aqueous solution in its
general characteristics, but when proper concentrations are
used so as to bring out the fine bands it is found that the two
spectra are entirely different. For example, the aqueous solu-
tion shows a very fine band at $\lambda\,4274$. In the glycerol there
is a band that on first sight appears to be exactly identical with
this $\lambda\,4274$ band. However, its wave length is about $\lambda\,4287$,
and it has two extremely fine components on each side, one at
$\lambda\,4273$ and one at about $\lambda\,4300$. The same is true throughout
the spectrum.

In general, in mixtures of water and glycerol the appear-
ances indicate that there are "glycerol" bands and "water"
bands and as the amount of one solvent is increased, so are
the bands corresponding to this solvent increased in intensity.
Herein lies a very large field for investigation and considerably
more work is being carried on here along these lines. The
above described spectrum of the glycerol solution of neodym-
ium indicates that glycerol has a very great influence upon
the vibrations of the electrons within the neodymium atom,
and that this is due to a kind of "atmosphere" of glycerol
about the neodymium atom. Jones and Anderson showed
that alcohol has a similar effect, and that the "alcohol" bands

were much less persistent than the water bands. Further work is being done on the relative persistence of "water," "alcohol" and "glycerol" bands; also on the effects of foreign substances and rise of temperature on these bands, both in the pure solvent and for mixtures of solvents.

XI. Summary.

The absorption spectra of the uranyl salts contain a series of bands in the blue and violet. Twelve of these bands can usually be detected for each salt. Starting from the blue end of the series the bands are designated by the letters a, b, c, etc. These bands are usually diffuse and from 30 to 50 A. U. wide.

The uranyl bands of uranyl nitrate in water are all farther to the violet than the uranyl bands of any other salt investigated, or of uranyl nitrate in other solvents.

The uranyl absorption bands of crystals of uranyl nitrate agree with the absorption bands of an aqueous solution of the nitrate, with the exception of the f, g, h and i bands, these latter being shifted to the red in the crystal.

Dilution within the ranges studied does not affect the position of the uranyl bands. Theoretically, all the uranyl salts in water should give the bands of the same wave lengths for very dilute solutions.

The uranyl bands of the nitrate in methyl alcohol are all shifted to the red about 50 A. U. with reference to the bands in water. Mixtures of water and methyl alcohol show that we have both sets of bands existing for the same solution, the "water" bands increasing in intensity as the amount of water increases. The water bands are the more persistent. This indicates the existence of a hydrate and an alcoholate of the uranyl group. In ethyl alcohol the a, b, c and d bands are shifted to the red with reference to the methyl alcohol bands. The other bands appear to have the same positions as the methyl alcohol bands.

The absorption spectrum of the anhydrous salt is very complex and the bands could not be recognized.

The bands of uranyl bromide in water, of uranyl acetate in

water and methyl alcohol, and also of the anhydrous salt, are approximately of the same wave lengths, differing but slightly from the wave lengths of the uranyl nitrate bands of an aqueous solution.

The bands of uranyl sulphate in water are all shifted towards the red about 50 A. U. with reference to the uranyl nitrate bands in water. For both the sulphate and nitrate in water the bands are very much alike. The i band is very weak in both cases.

Uranyl chloride bands of an aqueous solution are shifted to the red with reference to the uranyl nitrate bands of an alcoholic solution. The addition of calcium chloride or aluminium chloride is found to produce very marked effects upon the uranyl chloride bands. The addition of sufficient aluminium chloride to a water solution of uranyl chloride, or of calcium chloride to a methyl alcohol solution of uranyl chloride, is found to cause the d and e bands to come together, so as to form a single wide band, and to cause the other uranyl bands to shift so that the whole resulting series of bands is almost identical with the series of bands of an ethyl alcohol solution of uranyl chloride. The effect of adding foreign substances also greatly modifies the intensity of the bands. An example of this difference of action is the effect of adding aluminium chloride to an aqueous solution of uranyl chloride. The a and b bands are affected entirely differently, the a band being very much reduced in intensity and made narrower, whereas the b band becomes very much stronger and wider.

A new set of fine bands in the green has been discovered in the absorption spectrum of an aqueous solution of uranyl chloride. These appear only for pure water solutions, a small amount of aluminium or calcium chloride causing them to vanish. They do not appear for methyl or ethyl alcohol solutions, nor for any other uranyl salt except very faintly for the sulphate.

The absorption spectrum of several uranous salts has been photographed. The spectrum is entirely different from that of the uranyl compounds. The absorption spectra of uranous chloride in methyl alcohol and in water were found to be very

different. The absorption spectrum of neodymium chloride in glycerol was found to be entirely different from that of the salt in water. For mixtures of water and glycerol there are indications of the existence of both sets of bands in the same solution. The "glycerol" bands are more persistent than "alcohol" bands with reference to water bands. Work is now being done on the relative persistencies of the various water, alcohol, glycerol, etc., bands.

The intensity of the phosphorescence of the same uranyl salts, obtained from different solvents by evaporation, is found to be very different. Monochromatic stimulation fails to excite phosphorescent bands until the wave lengths reach the region of the uranyl bands.

It is found that the NO_3 group has a very great influence on the frequency of the uranyl bands of absorption, of the uranous absorption bands and of the uranyl phosphorescent bands.

(*The second part of this paper will be published in the February number of* THIS JOURNAL.)

NOTE.

PECAN OIL.

This oil was prepared from the large cultivated pecans, which were kindly furnished us by Mr. E. Risien, of Rescue, Texas. The kernels made up 47.0 per cent. of the nuts, and contained 70.4 per cent. oil. The oil was extracted with ether, the ether evaporated, and the oil dried and filtered. It had a light straw color and a pleasant pecan odor and taste. The methods of examination are those described in Benedict and Lewkowitsch's "Oils, Fats, and Waxes." The figures given are the average of two determinations, as a rule. For purposes of comparison, the constants of olive oil, taken from the book referred to above, are given:

	Pecan oil.	Olive oil.
Specific gravity 15/15° C.	0.9184	0.916–0.920
Saponification value	198.0	185–196
Iodine absorption (Hübl's method)	106.0	77–88
Volatile acids (Reichert–Meissl value)	2.2	0.3
Acetyl value	1.16	. . . . .
Insoluble fatty acids, per cent. (Hehner value)	93.4	95
Lecithin, per cent.	0.5	. . . . .
Cholesterol, per cent.	0.28	0.46–1.00

The lead soap prepared from the fatty acids of this oil was completely soluble in ether, indicating the absence of saturated acids. Exposed to the air at room temperature, the oil gained 0.7 per cent. in weight in three days, after which it lost slightly. In a steam oven the oil gained in weight 0.65 per cent. in 4 days, after which it lost weight. As the oil had been previously freed from ether in a steam oven these values for oxygen absorption are probably low, but the oil evidently belongs to the nondrying class. Pecan oil resembles olive oil closely excepting in its iodine absorption value, which is near to that of beechnut oil or of cotton seed oil.

Calculated from the iodine value, the oil contains 24 per cent. linolin and 76 per cent. olein. But the fatty acids precipitated from the alkaline soaps with acid were solid at the room temperature, and altogether they melted in time, and when once melted did not solidify easily, yet it appears that this oil could not contain the amount of olein stated above, but must contain some other glyceride of a fatty acid having a higher melting point.

With the elaidin test a butterlike mass was formed which was not as solid as that obtained from olive oil.

TEXAS EXPERIMENT STATION.   A. C. DEILER AND G. S. FRAPS.

REVIEWS.

THE CHEMICAL CONSTITUTION OF THE PROTEINS. BY R. H. ADERS PLIMMER, D.Sc., Assistant Professor of Physiological Chemistry in, and Fellow of University College, London. In two parts. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1908. Part I, pp. xii + 100, price, $1; Part II, pp. xi + 66, price, 80 cents.

This essay forms a part of the admirable series of monographs on Biochemistry now being issued under the editorship of Messrs. Plimmer and Hopkins. "The Chemical Constitution of the Proteins" is naturally one of the most important of the various topics which are under consideration and this difficult subject has been admirably treated by Dr. Plimmer in the present volumes. The first part deals with the chemical composition of the protein molecule and of the numerous amino-acid units that are comprised in it; the second part is devoted to a consideration of the various syntheses of protein-like substances which have been successfully accomplished by Curtius, Abderhalden, and above all, by Emil Fischer.

The writer is acquainted with no account in the English language of the chemistry of the proteins comparable either

for completeness or accuracy with the one under review and the monograph should be of great value to a large number of organic chemists who wish for a presentation from a strictly chemical point of view of so important a subject.

FIRST PRINCIPLES OF CHEMICAL THEORY. BY C. H. MATHEWSON, PH.D., Instructor in Chemistry and Metallography at the Sheffield Scientific School of Yale University. First Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1908. pp. vii + 123. Price, $1.

The contents of this volume are as follows: Natural classification of the elements; determination of molecular weights; determination of atomic weights; calculation of formulas; osmotic pressure and related phenomena with particular reference to dilute solutions of acids, bases and salts; the electrolytic dissociation theory; the law of chemical mass action; heterogeneous equilibrium and phase rule; thermochemistry. The author's treatment of these subjects is thoughtful and thorough; the book should be helpful to students as a reference book or for careful study of theory, as much of the theoretical matter scattered through the pages of larger text-books is here condensed.

The author says in the preface that the book is for the use of first year students at the Sheffield Scientific School, as reference text in connection with a six weeks' course on chemical theory which immediately follows the first four months' instruction in general chemistry. Probably most teachers who examine the book will prefer to postpone its use until the student has completed the work of the first year.	E. R.

INTRODUCTION TO THE RARER ELEMENTS. BY PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. Second Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. pp. x + 207. Price, $1.50 net.

It is seldom that the second edition of a well-known book is so broadened and enlarged and withal improved as is the case with this work of Dr. Browning. It is almost as if an entirely new treatise had appeared and we may well be glad that it is printed in the English language, for we have sadly needed an available book for student reference and use. These rarer elements, too often neglected in the curricula of our colleges and universities, can no longer be passed over for lack of an available text. By its appearance encouragement is sure to be given to study in this charming section of inorganic chemistry and even chemists who are no longer students might well perform many of the well chosen experiments and increase their knowledge at first hand of these elements of which we all know too little. Dr. Browning has

done his work well. The book covers 206 pages of description and experiments. Only lists of chief compounds are given and it is to be hoped that in future editions enlargement may be along the line of description of these compounds, their relative solubilities, etc. The methods of separation can, at least in most instances, be depended upon as the latest and best. To the reviewer the chapter on the rare earths is especially worthy of mention for its clearness of diction, its list of mineral sources, its classification and for carefully selected and described methods of separation. The chapter on the rare gases of the atmosphere and the chapter written by Dr. Boltwood on the radioactive elements are worthy additions which give the book completeness and added value, and the inclusion on the final pages of the qualitative scheme of separation of these rarer elements of Noyes, Bray and Spear, and that of Böhm, will give ready reference to these latest and best identification methods.

It is seldom that the reviewer has a pleasanter task than this book affords, for there is so little to criticize and so much worthy of praise. The book should be in the hands of every chemist. Charles L. Parsons.

Glass Manufacture. By Walter Rosenhain, B.A., B.C.E., Superintendent of the Department of Metallurgy and Metallurgical Chemistry at the National Physical Laboratory, New York. D Van Nostrand Co., 1908. pp. ix + 264. Price, $2.

Hitherto it has been difficult for general students to get the kind of information desired about glass. In the text-books of technical chemistry the information is too meagre, in the larger books too diffuse and too much specialized. This present book supplies this want. Mr. Rosenhain is an expert, and writes a very interesting book, and writes it for the users, not for the makers of glass.

The book describes the chemical and physical properties of glass, raw materials, crucibles and furnaces, the various processes, bottle glass, blown and pressed glass, plate glass, crown glass, colored glass, optical glass, the theoretical requirements of optical glass and the attempts to meet these requirements by the work of Abbé and Schott of Jena. The account of the Jena glasses is particularly interesting. Mr. Rosenhain's book should find plenty of readers as it is the only one of the kind. E. R.

Die Lack und Firnisfabrikation. von Professor Max Bottler, in Würzburg. Mit 29 Abbildungen im Text. Halle a/S.: Verlag von Wilhelm Knapp. 1908. pp. ix + 130. Price, M. 4.50.

This is a little book of about 40,000 words, covering the

whole subject of oil-varnish, oleo-resinous and spirit varnishes, their components and manufacture. It is necessarily brief and incomplete, but is designed to give information of materials and processes which are up to date, at least in Germany. It is not a book of formulas. After a few introductory pages, chiefly of definitions, materials used in varnish-making are described; one-fourth of the book is devoted to resins and the like, including such widely varying substances as rubber, camphor, spermaceti and pyroxylin, a brief, but on the whole, satisfactory chapter; the classification of copals is open to criticism, but probably no one could make such a presentation which would not be; it is really about time for those interested to get together and agree on some standards, no matter how arbitrary they may seem. As it is, every one is a law unto himself. Brief notices of drying oils follow, amounting to half a dozen pages. The statement is made that flaxseed contains 60 per cent. oil and yields by ordinary hot-pressing 28 per cent. As a matter of fact, the oil content varies from 37 per cent. (South American) to 42 per cent. (Calcutta), and the actual yield is from 32 to 33 per cent. While some German writers give the actual yield as low as 26, this is based on an estimate of about 37 per cent. total oil in European seed, so that on this point the author must be in error. Eight pages are given to turpentine, alcohol and other volatile solvents; lead and manganese compounds (catalyzers) are briefly described; then nearly half the book is given to apparatus and processes. This is illustrated with many pictures, most of them of apparatus now in use, of much interest; and the whole chapter will repay careful reading, being, in fact, open chiefly only to the objection that it is incomplete, which applies to the whole book. Spirit varnishes have relatively more space than others, and this chapter is especially good. There is a short section on bleaching and filtering. The book contains comparatively few references, but shows familiarity with recent work; it is for the casual student and the general reader, and such will find it useful and interesting.   A. H. SABIN.

ELECTRO-METALLURGY. By JOHN B. C. KERSHAW. With 61 Illustrations. New York: D. Van Nostrand Co. 1908. pp. xv + 303. Price, $2.

The author states in his preface that the book has been prepared for readers who have but a slight acquaintance with chemistry and electricity. The aim must be therefore to cover the ground in a general way, and to make the reading pleasant and attractive. This the author has done well; he

has described briefly the leading processes and has given the principal facts about the foremost plants so far as they are generally known; he also holds the interest of the reader. The book covers the metals aluminum, silver, gold, copper, iron, lead, nickel, tin and zinc; the elements calcium, magnesium, phosphorus, silicon and radium; it also discusses calcium carbide and acetylene gas, carborundum, glass, quartz-glass, graphite, carbon bisulphide and tetrachloride, and diamantine. Thus subjects are dealt with which lie outside of the usual range of electro-metallurgy. There are a few slips here and there, but the whole is accurate in the subjects with which the reviewer is familiar. Within the lines drawn by the author, the book will prove eminently satisfactory.   H. O. HOFMAN.

RAPID METHODS FOR THE CHEMICAL ANALYSIS OF SPECIAL STEELS, STEEL-MAKING ALLOYS AND GRAPHITE. BY CHARLES MORRIS JOHNSON, Chief Chemist to the Park Steel Works of the Crucible Steel Company of America. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. vii + 221. Price, $3.

The author in his preface calls attention to the accounts of the methods which he originated and the investigations which he pursued to simplify and expedite the analysis of special steels and steel-making alloys. For this work he certainly deserves great credit, especially for the modifications he suggests in the method for the direct determination of nickel in steel and for the method for the determination of phosphorus in ferro-vanadium. In the former method the direction to use a 20 per cent. solution of potassium iodide is probably a misprint. The qualitative tests for the presence of vanadium, chromium, tungsten, and molybdenum in steels are useful and practical. It is impossible within the limits of an ordinary review to criticize the methods in detail, but it may be remarked that many of those described for the analysis of pig irons and ordinary steels are not the methods generally considered the most accurate. The method for the volumetric determination of manganese is neither as accurate nor as rapid as the bismuthate method, and the volumetric method for sulphur with an admitted variation of 25 per cent., while it undoubtedly has its sphere of usefulness, is not apt to be accepted by the buyer and seller of pig iron, as suggested by the author, however well its limitations may be understood.

Kopp's method for the determination of molybdenum in molybdenum powders is to be preferred to either of the methods given in this book, and Gooch's modified method

for the determination of titanium is far preferable to the one here recommended.

In the manipulations described in great detail the directions to wash a precipitate 40 or 50 times do not seem to make for rapidity, although this may be necessary when the precipitate is mixed with 50 cc. of paper pulp. Apart from the methods themselves the descriptions are usually clear and easily followed, but the departures from the strict rules of grammatical construction are frequent, and the constant use of what may be called "chemical slang" is really distressing. Such expressions as "evaporate to a scum," "wash free from chloride test," "evaporate the samples to fumes," do not seem suitable in a work of this character.

ANDREW A. BLAIR.

AMERICAN

CHEMICAL JOURNAL

THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION AND THE EFFECT OF TEMPERATURE ON SUCH SPECTRA.[1]

By Harry C. Jones and W. W. Strong.

PART II.—THE EFFECT OF RISE IN TEMPERATURE ON THE ABSORPTION SPECTRA OF VARIOUS SALTS IN AQUEOUS SOLUTION.

Outline.—I. Review of Recent Spectroscopic Investigations. (*a*) Spectra of Gases and the Mechanism of the Light Vibrators. (*b*) Spectra of Liquids and Solids. (*c*) The Absorption of Banded Spectra. II. The Zeeman Effect. III. The Effect of Rise in Temperature on Absorption Spectra. (*a*) Cobalt Salts. (*b*) Nickel Salts. (*c*) Copper Salts. (*d*) Chromium Salts. (*e*) Uranium Salts. (*f*) Praseodymium Salts. (*h*) Erbium Salts. IV. General Results.

Description of Plates.

Plate IX. Cobalt Chloride.—A. 2.37 normal, 1.3 mm. B. 0.31 normal, 10.4 mm.

Plate X. Cobalt and Aluminium Chlorides.

Plate XI. Nickel Acetate.

Plate XII. Copper Bromide. 2.16 normal, 1 mm.

[1] Part I of this paper was published in This Journal, **43**, 37.

The study of the various phenomena of light may be divided into three parts: The emission of light by matter, the transmission of light through space and the absorption of light by matter. The theory of the transmission of light as an electromagnetic phenomenon was first proposed by Faraday and Maxwell. On this theory it is assumed that in all regions of space through which light passes there are electric and magnetic fields. In an electric field there exists a certain state of things that gives rise to a force acting on any electric charge that may exist there. This is the electric force and this represents the state of the region of space considered. In a similar way the magnetic field is also defined. A relation is then found between the electromagnetic quantities which is usually called Maxwell's equations, or is a modified form of these equations. Starting with these equations Maxwell showed that the state of things represented by his fundamental equations consists of the propagation of a periodic variation of the electric and magnetic forces through space with the velocity of light. So well do the nature of these electromagnetic waves agree with the properties of light as transmitted by the ether and transparent bodies that light is at present considered to be an electromagnetic disturbance itself. The simplest case of light waves is that of plane polarized waves traveling in the direction of the x axis. Waves of this kind are:

$$E_y = a \cos n\left(t - \frac{x}{c}\right), \; H_z = a \cos n\left(t - \frac{x}{c}\right).$$

E_y, the component of the electric force in the y direction, is the only component of the electric force that has a value. The magnetic force has a component only in the z direction, H_z. a is the amplitude of the disturbance, t is the time, n is the number of vibrations in a time 2π and c is the velocity of light.

I. Recent Spectroscopic Investigations.

A light wave in the "ether" is an electromagnetic disturbance that is propagated in free space without any distortion of form or any dissipation of energy, one of the properties of electric and magnetic fields being the power to store energy. When a light wave strikes ordinary matter it is in general broken up into several parts. If the surface of the body is smooth, a considerable part of the energy will be taken up by a regularly reflected wave. If the surface is rough, a great number of so-called waves will be reflected. The remaining part of the disturbance will advance through the body. As no body is a perfect reflector or absolutely transparent, it follows that part of the energy of the light wave remains with the body. This phenomenon is known as the absorption of light. We also know of many conditions of matter in which light is emitted. The object of the study of emission and absorption of light is to gain some knowledge of the mechanism of matter by which it is enabled to produce or absorb electromagnetic waves. The expression of the properties of different kinds of matter by different values of the dielectric constant (κ), the conductivity (σ) or the magnetic permeability (μ) has not been found to be satisfactory.

The electromagnetic mechanism which at present is considered as the basis of the theories of radiation and absorption is the electron. The charge which it carries has been found to be the atomic unit of electricity. Experimental results in electricity can be explained on this basis. The electron is found in the vacuum discharge tube, in the radiations from radioactive matter, in arcs, in sparks, in secondary radiations. They are present in all bodies. By the distribution and motions of these electrons scientists of to-day at-

tempt to explain all electrical and optical phenomena. Some electrons in a conducting body are in a free state so that they can obey an electric force. Richardson and Brown[1] have shown that ions emitted by hot platinum (and approximately so for other metals) are kinetically identical with the molecules of a gas, of equal molecular weight, at the temperature of the metal. This holds for the mode of distribution of velocity as well as its average value. This shows that the free electrons inside the metal have the same amount and mode of distribution of velocity and kinetic energy as the molecules of a gas of equal molecular weight at the temperature of the metal.

In the case of a nonconducting substance the electrons are considered as bound to certain positions of equilibrium. In a conductor in an electric field there is an excess of electrons at one end. In a dielectric, as soon as an electron is displaced from a position of equilibrium, a new (elastic) force is brought into play which pulls the electron back to its original position. The motion of electrons in nonconducting bodies, together with the change of dielectric displacement of the ether itself, makes up Maxwell's displacement current. Under the influence of the elastic forces the electrons can vibrate about their positions of equilibrium and may thus become the centers of electromagnetic waves. In this way may be explained the emission of light and heat. Absorption results when the electrons are set into vibration by a beam of light and part of the vibrating energy of the electron is transformed into heat energy.

As to the nature of the electron very little is known. On the other hand, the mathematical electron is much better known. As the recent experiments by Bucherer[2] on the value of e/m agree with values calculated by Lorenz, use will be made here of his conception of the electron. To each electron is ascribed certain definite dimensions. The ether is assumed to pervade not only the space between atoms but also the space within atoms and electrons. This ether is assumed to

[1] Phil. Mag., Sept., 1908; Dec., 1908.
[2] Physik. Z., Nov., 1908, p. 755.

be at rest. There will be an electromagnetic field within the electron as well as without. Various distributions of charge may be assumed. Lorentz usually assumes a volume density (ρ) distribution such that ρ is a continuous function of the coördinates. The charged particle has then no sharp boundary but is surrounded by a thin layer in which the density gradually sinks from ρ to o. The ether is simply the space in which a certain state of the electromagnetic field exists. (Recently very interesting papers by Einstein and others on this subject have appeared.) The electron having been thus defined, equations can be formed for the electric and magnetic fields for any region in which there are electrons either at rest or in motion. Having considered the elementary unit of the mechanism of optical phenomenon let us now turn to some of the phenomena themselves.

(*a*) *Spectra of Gases.*—For optical purposes bodies may be divided into gases and into solids and liquids. The spectra of gases consist of an enormous number of fine lines and are usually grouped into line and band spectra. Band spectra themselves consist of a great number of sharp lines spaced in a very regular manner, whereas line spectra consist of lines apparently spaced more or less at random in the spectrum although some of the lines have been found to have frequencies that are connected by certain series relations. Good examples of band spectra are the absorption spectra of fluorine, bromine, iodine, chlorine, sulphur or sodium vapors. These consist of thousands of very fine lines. Very interesting work has recently been done by Wood on the magnetic rotation spectrum and the fluorescent spectrum of sodium vapor. On exciting fluorescence by monochromatic light of different wave lengths it is possible to set into vibration apparently different systems in the sodium atoms or clusters containing sodium atoms, each one of these systems of vibrators emitting a different series of bands. It is found that the presence of foreign gases has a very great effect upon the absorption spectra of sodium. The presence of hydrogen prevents fluorescence. Wood[1] found that as mercury vapor is evolved in

[1] Astrophys. J., **26,** 41 (1907).

a vacuum the band $\lambda\,2536$ broadens rapidly on the less refrangible side, attaining a width of three or four hundred A. U. There is a little broadening in the other direction. If hydrogen or some other inert gas is present, the band broadens symmetrically at first. Larmor[1] has suggested that this unsymmetrical widening may be due to the formation of loose molecular aggregates, which vibrate in longer periods owing to this mutual influence. Wood and Guthrie[2] find that the cadmium absorption band $\lambda\,2288$ broadens symmetrically in the case of pure cadmium but very asymmetrically when mercury is present. A very promising field for research is suggested by this work, one that will probably throw much light upon the mechanism within the atoms themselves.

Quite recently Dufour[3] has succeeded in obtaining the Zeeman phenomena for many of the bands of the emission spectrum of fluorides and chlorides of calcium, strontium, barium and silicon. These give in some cases a normal and in other cases an abnormal longitudinal Zeeman (light being parallel to the magnetic field) doublet, the normal doublet usually being considered as originating from a negative charge and an abnormal doublet as due to a positive charge. The only difference in these two effects is that the light is circularly polarized in opposite directions for corresponding components of the doublet. Dufour considers that so far all spectra (emission or absorption) that show the abnormal Zeeman effect have their centers in the molecules. If one considers the explanation to be due to positive and negative electrons, then the value of e/m for these will be about the same except in the case of some of the bands of xenotine. At the University of Manchester it has been shown that the Humphrey-Mohler pressure shift is to be observed for bands that give the Zeeman effect. With the exception of the few bands described by Dufour, the wave length of bands is unalterable by physical and chemical changes.

The band spectra are very complex indeed. In Watts'

[1] Astrophys. J., **26**, 120 (1907).
[2] *Ibid.*, **28**, 211 (1909).
[3] Physik. Z., **4**, 124 (1909).

"Index to Spectra" the wave lengths of over 5000 bands are given for sulphur between λ 6400 and λ 3600, over 2700 lines for iodine between λ 6300 and λ 5100, over 2800 for bromine between λ 6200 and λ 5100, and over 2600 for aluminium oxide between λ 5200 and λ 4400. Complex as these spectra are, the so-called line spectra of the elements are even more complex. The same author gives the wave lengths of over 2300 lines for chromium, 3000 for iridium, 2300 for iron (spark), 3000 for tungsten (spark), and 5200 for uranium (spark). For most of these elements the greatest number of lines lie in the regions of shorter wave lengths, and in most cases the maximum number of lines lie between λ 4000 and λ 3000. For example, Watts gives 1100 iron lines between $\lambda\lambda$ 2000 and 3000, over 1400 lines between $\lambda\lambda$ 3000 and 4000, 1100 lines between $\lambda\lambda$ 4000 and 5000, over 600 lines between $\lambda\lambda$ 5000 and 6000, and only a little over 300 between $\lambda\lambda$ 6000 and 6750. A similar distribution holds for vanadium, osmium, etc. The work of Schumann and Lyman shows that many more lines exist in the ultraviolet down to λ 1000, but it seems quite probable that most of the spark and arc lines lie either in the visible or in the adjacent ultraviolet regions of the spectrum.

When the source of the line spectrum is subjected to physical changes the width and relative intensities of the bands change enormously. Rayleigh[1] and Michelson[2] have shown that the Döppler effect accounts for the width of the lines when the pressure is small. Michelson gives a formula for the breadth (b) of the spectrum lines,

$$b = \sqrt{\theta m} \; \lambda(a + bd\lambda),$$

where θ is the absolute temperature, m the molecular weight, a and d constants.

At present only two physical causes are known to change the frequency of vibration of the emitters or absorbers of the line spectrum. One of these is the Humphrey-Mohler effect— that an increase of pressure about the source of light causes

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[1] Phil. Mag., **27**, 298 (1889).
[2] *Ibid.*, **34**, 280 (1892).

the lines to be slightly shifted towards the red. Humphreys considers this to be due to the magnetic fields of neighboring atoms. Richardson,[1] on the other hand, considers the shift as due to electrostatic action. An increase of the partial pressure of the vapor of the emitting substance only causes the lines to widen. An increase of the total pressure of the surrounding vapor causes a shift, and this Richardson considers as due to sympathetic vibrations set up in the surrounding atoms. If an atom is emitting light it must be surrounded by an alternating field of force and this will produce forced vibrations of equal period and, under certain conditions, of equal phase in the neighboring atoms. These sympathetic vibrations will then react upon the emitting atom and increase its period. After making several assumptions as to the vibrator in the emitting atom, Richardson deduces a shift which is considerably larger than that observed.

The second phenomenon of the change of frequency of line spectra is that of the Zeeman effect. Many lines show a simple Zeeman effect such as would be produced upon a vibrating negative electron. Other lines show a very complex Zeeman effect which as yet has not been fully explained. Still other lines show no Zeeman effect at all. All line spectra show a Zeeman effect that indicates that the vibrator carries a negative charge. Series lines usually show a similar resolution in a magnetic field as well as a similar behavior under variations of pressure, temperature, etc. Very important discussions of the Zeeman effect by Lorentz, Voigt, Ritz, etc., have recently appeared.

Some very interesting work has recently been done by Lenard,[2] Stark,[3] and others on the carriers of matter that are emitting light. In vacuum tubes, in arcs, in flames and in the radiations from radioactive bodies we have electrons, atoms, molecules, charged atoms or molecules or aggregations of these that are moving in some cases with very great velocities. The free electron, as we shall see, radiates a continuous spec-

[1] Phil. Mag., Nov., 1907.

[2] Ann. Phys., **9**, 642 (1902); **11**, 649 (1903); **12**, 475, 737 (1903).

[3] *Ibid.*, **14**, 506 (1904), etc.

trum, but the bound electron, being disturbed comparatively infrequently by collisions of the atom in which it is bound, will emit more or less monochromatic radiations. Now in the case of flames, arcs, etc., it is possible to separate the positively and negatively charged ions by means of an electric field.

Lenard's work indicated that the radiators of line spectra were either neutral atoms or positive ions, the principal series being due to neutral atoms, and the subordinate series to positively charged atoms. If an ion has a swarm of molecules about it, it is unable to radiate or absorb. Stark studied the Döppler effect of canal rays in vacuum tubes. He found that in the case of a beam of light coming from the canal rays in the same direction in which they are moving many spectrum lines showed a "rest" line and a displaced line due to the Döppler effect. He found that some series lines consisting of doublets originate from univalent positive ions and the mercury triplets start from divalent positive ions. Some lines show no Döppler effect and these originate from a negative electron joining a positive ion. The displaced line is separated from the normal line by a dark space which is found to be wider the smaller the wave length of the line. Assuming that there are particles of varying velocities in the canal rays, Stark concludes that a certain velocity is necessary before a particle begins to radiate light appreciably. Stark thus considers velocity of translation as one cause of radiation. The other cause of continuous radiation of energy by an atom is frequent collision with electrons or other charged atoms.

So far no satisfactory model has been devised that will act as a source of spectrum lines. No system that includes electrical charges in orbital motion is permanent on account of their radiation of energy. The favorite and best model consists of systems of coaxial circular rings of equidistant electrons, but even in this case Schott[1] has shown that such a model (in particular that of Nagaoka), although giving a

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[1] Phil. Mag., April, 1908, p. 438.

large number of spectrum lines, is too unstable to produce wave trains of sufficient length.

Stark has recently suggested the possibility of explaining a positive charge as due to negative electrons revolving in circular orbits, the centers of these circular orbits being themselves on a circle. By means of such a device a positive charge can easily be explained. He thinks that line spectra originate from a system of this kind. The general trend[1] of opinion seems to favor the view that spectrum lines are due to some special mechanisms in the atom which are set in operation during ionization and operate for only a short time. At any one time the atom may be radiating light of but one frequency.

(*b*) *Spectra of Liquids and Solids.*—The optical phenomena of gases are so much better understood on account of our more perfect knowledge of gases that considerable space has been given to their discussion. On the other hand, the conditions in liquids and solids are so exceedingly complex that at present our theories are in the main very crude. Considerable advances in our experimental knowledge of these phenomena have recently been made and a short summary of these will be given.

The spectra of liquids and solids can be roughly divided into the continuous spectra emitted by very hot liquids or solids, secondary X-ray radiations, phosphorescent or fluorescent spectra and the absorption or emission of a banded spectra.

According to the present theory, X-rays, and possibly γ-rays, and the continuous spectra from hot liquids and solids are due to a rapid and irregular succession of sharp electromagnetic pulses, each of which is due to the change of velocity of electrons. Recent work on X- and γ-rays indicates that in most bodies a certain homogeneous secondary radiation is excited when the body is exposed to the X- and γ-rays. This secondary radiation seems very similar to the phosphorescent

[1] J. J. Thomson: "The Corpuscular Theory of Matter," 1907. Ladenburg and Loria: Nature, **79**, 7 (1908). Eagle: *Ibid.*, **79**, 68 (1908).

bands of the compounds investigated by Lenard and Klatt[1] and others. Lenard and Klatt[1] consider that electrons can exist in three different states—in a free state, as in the metals where they take part in conduction; a "liquid" state where there is a state of motion sensitive to light vibrations; and a "solid" state where the electrons take part in neither conduction nor the absorption of light. They consider that in the states of aggregation which cause phosphorescent bands there are certain places in the atoms, dynamids, where electrons can be stored at low temperatures. To each phosphorescent band there correspond then these phases: (1) an upper momentary or heat phase; (2) a permanent phase; (3) and a lower or momentary phase. For a great many bands they succeed in obtaining these three phases when they change the temperature sufficiently. The temperature of solid hydrogen is sufficiently low to bring most of the phosphorescent bands into the lower momentary phase. In this phase the electrons ejected from the metallic atom by photoelectric influence of illumination are fixed and stored in the neighborhood, only a few returning immediately, and these produce the "momentary light" observed during illumination. In the permanent phase the electrons are stored for a certain time in the dynamids and eventually return to the metallic atom.

Various theories have been proposed to explain the more or less general absorption throughout large regions of the spectrum. Drude[2] considers that in general ultraviolet bands are due to the absorption of electrons, and infrared bands to the absorption of ions. Houstoun,[3] Pfund[4] and others support this view.

(c) *Banded Spectra.*—By banded spectra we shall in general designate bands which at low temperatures become quite fine, such as the uranyl, neodymium or erbium bands. As the present paper deals with only a small range of temperature and concentration and but one solvent, a full review

[1] Ann. Phys., **15**, 451 (1904).
[2] *Ibid.*, **14**, 677–725, 936–961 (1904).
[3] P. Roy. Soc., Sept., 1909, p. 606.
[4] Astrophys. J., **24**, July, 1906.

of previous work will not yet be given. Rudorf[1] and Washburn[2] have given a very good review of this subject from the hydrate point of view.

Brewster observed, in 1831, that the transparency and color of many solids changes when they are heated. Schönbein, in 1852, states that many bodies become more highly colored at higher temperatures while at low temperatures they lose their color. He found that sulphur is colorless at —50° C. and bromine at —70° C. Moissan and Dewar, in 1903, found that fluorine becomes colorless at —253°, so that at low temperatures chlorine, bromine, iodine and fluorine are colorless.

Conroy (1891) found that the bands of cobalt glass are displaced towards the red with rise in temperature. Rizzo (1891) found similar results with glasses containing cobalt, didymium and manganese. Königsberger (1901) found the curve of absorption to be displaced towards the red with rise in temperature, but concluded that the maximum of absorption was not changed. This applied to the wider bands. The fine bands showed no displacement between 10° and 500° C. Hartley investigated the absorption spectra of a large number of solutions between 0° and 100°. He interpreted his results from the point of view of hydration. Houstoun investigated the bands of glasses containing uranium and neodymium but found no shifts of the bands.

Very important papers on this subject have been published by Becquerel, Ritz, Retschinsky, Stark, Bois and Elias, Königsberger and Kilchling, Page, Laub, Voigt, and others.

II. *The Zeeman Effect.*

An effort was made to obtain the Zeeman effect for the absorption bands of uranyl chloride and neodymium salt solutions. An account of the experimental arrangement was given in the introduction. At present no effect has been obtained, but it is hoped that in erbium solutions this may be possible. Most of the bands for which Becquerel found large

[1] Jahrb. Rad. u. Elek., **3**, 422 (1906); **4**, 380 (1907).
[2] *Ibid.*, **5**, 493 (1908); **6**, 69 (1909).

Zeeman effects were due to erbium. Besides it may be possible that the presence of foreign substances modifies the Zeeman effect.

III. Effect of Rise in Temperature on the Absorption Spectra.

In discussing the various spectrograms that show the effect of change in temperature on the absorption spectra of salts, these spectra will be divided into three kinds:

The first kind of absorption consists of wide bands, in many cases hundreds of A. U. wide. In many of the spectrograms only one edge of the band may appear, the other edge of it lying in parts of the spectrum to which the photographic film is not sensitive or to which the spectroscopic apparatus is not properly adapted. Examples of this kind of absorption are given by the copper or nickel salts, the ferricyanides, the chromates, etc. There is not the slightest indication of a finer structure to these bands.

The second kind of absorption spectra consists of diffuse bands that are quite narrow in many cases and are usually very weak at ordinary temperatures. These bands may be from ten to several hundred A. U. wide, and at very low temperatures may be broken up into finer and sharper bands. Examples of this kind of bands are the cobalt, uranyl or uranous bands. In many cases these bands appear only under very special conditions of concentration and depth of cell. If the amount of absorbing material is large, there is usually a wide absorption band in the region. This is well illustrated by the uranyl bands and the blue-violet band of the uranyl salts. If the amount of absorbing material is small, the transmission of light is so great that these faint bands are entirely obliterated.

The third class of bands are sharp and appear over rather wide ranges of concentration. They are exemplified by the neodymium and erbium bands. This classification of bands is quite suitable for the present article on account of the salts studied and the temperatures used. It is quite probable, however, that the latter two kinds of bands gradually merge into each other.

Cobalt Chloride.—A spectrogram, Plate IX, A, of the absorption spectrum of an aqueous solution of cobalt chloride was made for a 2.37 normal concentration and a depth of cell of 1.3 mm. The length of exposure was 3 minutes, current 0.7 ampere, and slit width 0.20 mm. Although there is transmission in the ultraviolet, no exposure was made to the spark in this instance, as this was the first salt worked with and the method of taking spectrograms had not as yet been fully perfected. Starting with the strip nearest the numbered scale, the temperatures were 1°.7, 14°, 30°, 45°, 56°, 72° and 81°.

At the lowest temperature there is an absorption band from λ 4800 to λ 5100. As the temperature rises this absorption band widens, slowly at first. At 56° it extends from about λ 4700 to λ 5600. At higher temperatures the increase in absorption in the red end of the spectrum is enormous and at 81° very little light is transmitted in this end, and for this reason the color of the solution becomes intensely blue. At 81° the absorption band runs from λ 4700 to λ 5700. From λ 5700 to λ 6000 there is a weak transmission. From λ 6000 on as far as the films are sensitive there is almost complete absorption. The bands $\lambda\lambda$ 6315 and 6440 appear at 72° and 81°. At lower temperatures the transmission is so great as to obscure these bands completely.

Several spectrograms were made of the absorption spectra of aqueous solutions of cobalt chloride of different concentrations. The time of exposure to the Nernst glower was the same for the three spectrograms, 3 minutes, the current being 0.7 ampere and the slit width 0.20 mm. The concentrations and depths of layer were as follows: 2.37 normal concentration, 1.3 mm. depth of layer and 2°, 15°, 30°, 45°, 58°, 73° and 81° (Plate IX, B); 0.315 normal concentration, the depth of layer 10 mm. and the temperatures —2°, 14°, 30°, 44°, 60°, 75° and 81°; 0.037 normal concentration, 83 mm. depth of layer and temperatures —0°.5, 14°, 30°, 45°, 60°, 70° and 81°.

The effect of concentration on the changes, due to rise in temperature in the absorption spectrum of a salt in solution,

Plate IX.

B   A
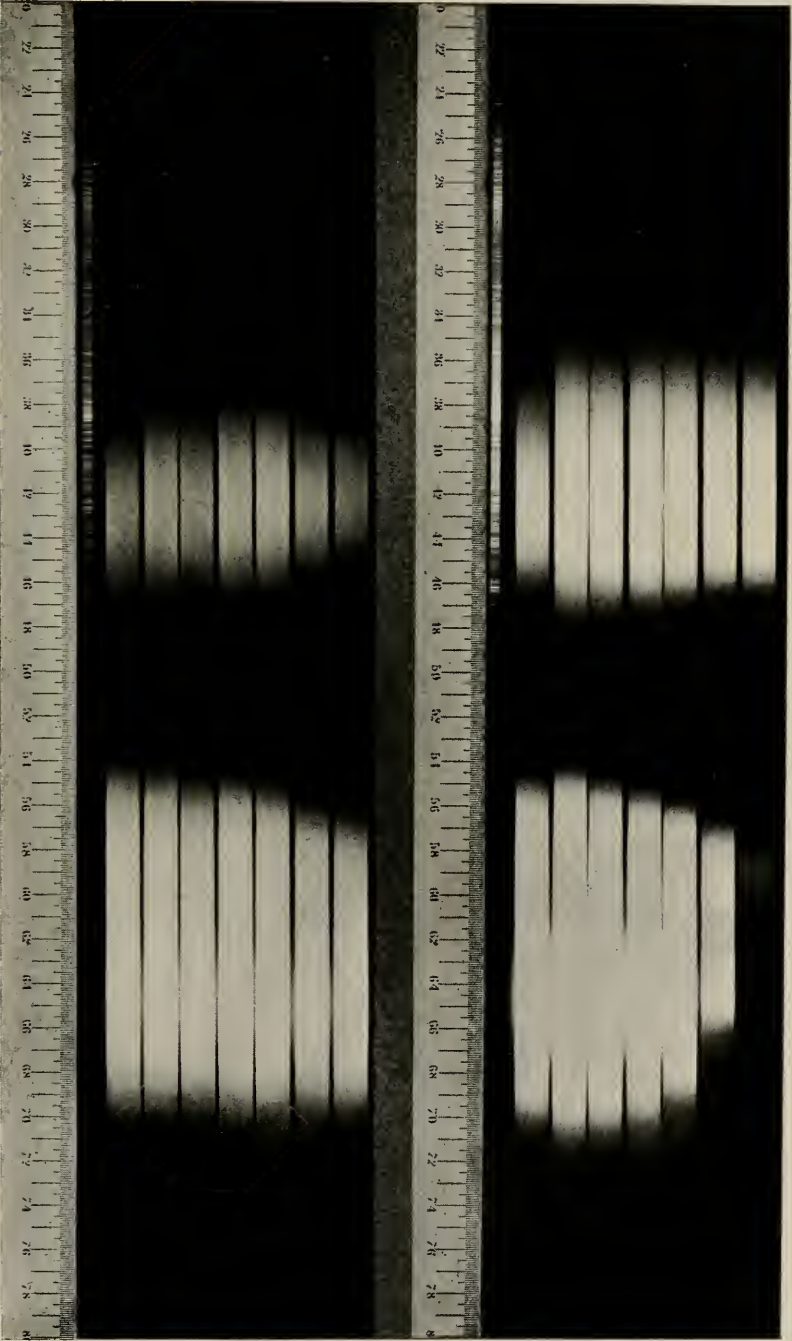
is brought out in these three spectrograms. For the most concentrated solution the yellow band at 2° runs from λ 4850 to λ 5400. There is a very intense action on the photographic film throughout the red. As the temperature rises the yellow band widens gradually and at 81° it extends from λ 4700 to λ 5700. At the higher temperature the whole red region is practically absorbed and the cobalt bands $\lambda\lambda$ 6100, 6250 and 6400 disappear. At 75° the cobalt bands showed faintly in a region of strong transmission between λ 5600 to λ 6650.

Cobalt Chloride and Aluminium Chloride.—A spectrogram, Plate X, A, was made to test the effect of rise in temperature on the change in the absorption spectra of a dilute solution of cobalt (0.00316 normal) in a concentrated 3.06 normal solution of aluminium chloride in water. The length of layer was 150 mm. The time of exposure was 2 minutes to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures were 1°, 18°, 41°, 55°, 68° and 85°.

The effect of rise in temperature in this case was greater than in that of a more concentrated solution of cobalt chloride. There is absorption in the whole violet region, so that the spectrum at 1° consists simply of a transmission from λ 4000 to λ 6500. The transmission is weak from λ 6100 to λ 6500 and shows the cobalt bands at $\lambda\lambda$ 6100, 6350 (about 100 A. U. wide) and 6420. At 18° the transmission band runs from λ 4000 to λ 6050. With rise in temperature the transmission band narrows and at 85° extends only from λ 4300 to λ 6750. Weak bands about 100 A. U. wide appear at $\lambda\lambda$ 5050 and 5300. These are considerably broader at the lower temperatures.

Cobalt Chloride and Calcium Chloride.—A spectrogram, Plate X, B, was made to show the effect of rise in temperature on the absorption spectra of a 0.0095 normal cobalt chloride and 4.6 normal calcium chloride solution in water. The depth of the layer was 50 mm., the length of exposure to the Nernst glower 3 minutes, the current 0.7 ampere and the slit width 0.20 mm. The length of exposure to the spark was

5 minutes. The temperatures, starting with the strip adjacent to the comparison scale, were $-1°.5$, $20°$, $30°$, $45°$, $57°$, $74°$ and $88°$.

The ultraviolet absorption reached to about $\lambda\,3000$, with a great deal of general absorption throughout the violet. This general absorption increased slightly with rise in temperature. At $-1°.5$ there was transmission to $\lambda\,6900$, and at $20°$ to $\lambda\,6800$. At $20°$ and $30°$ the cobalt bands show quite strongly at $\lambda\lambda\,6100$, 6240, 6400. At $45°$ the absorption reaches to $\lambda\,6050$, at $57°$ $\lambda\,5950$, at $74°$ $\lambda\,5850$ and at $88°$ $\lambda\,5800$.

Wide bands appear at approximately $\lambda\,5000$ and $\lambda\,5300$. These bands are very weak, considerably weaker than for a solution of cobalt chloride and aluminium chloride.

Cobalt Sulphocyanate.—A spectrogram was made to show the effect of change of temperature on a 2-normal aqueous solution of cobalt sulphocyanate $(CoS_2C_2N_2)$, 1 mm. deep. The length of exposure was 3 minutes to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale, the temperatures were $3°$, $18°$, $31°$, $45°$, $59°$ and $80°$.

Under these conditions of concentration and depth of layer the cobalt sulphocyanate absorption consists of an ultraviolet absorption band and a wide band in the yellow and green. As the temperature is raised these bands both widen out on the red side. The effect of temperature is especially marked between $60°$ and $80°$. The limits of the ultraviolet absorption are $\lambda\,3400$ at $3°$, $\lambda\,3450$ at $18°$, $\lambda\,3450$ at $31°$, $\lambda\,3500$ at $45°$, $\lambda\,3550$ at $59°$, and $\lambda\,3600$ at $80°$.

For the yellow-green band the limits are $\lambda\,4550$ to $\lambda\,5600$ at $3°$, $\lambda\,4550$ to $\lambda\,5630$ at $18°$, $\lambda\,4550$ to $\lambda\,5650$ at $31°$, $\lambda\,4570$ to $\lambda\,5700$ at $45°$, $\lambda\,4550$ to $\lambda\,5750$ at $59°$, and $\lambda\,4550$ to $\lambda\,6400$ at $80°$. At $59°$ there is a weak and broad band extending from $\lambda\,6000$ to about $\lambda\,6300$.

The remarkable feature of this spectrogram is that the yellow-green band widens only on the red side.

A spectrogram was made of a much more dilute solution of cobalt sulphocyanate in water, the concentration being

Plate X.

B   A
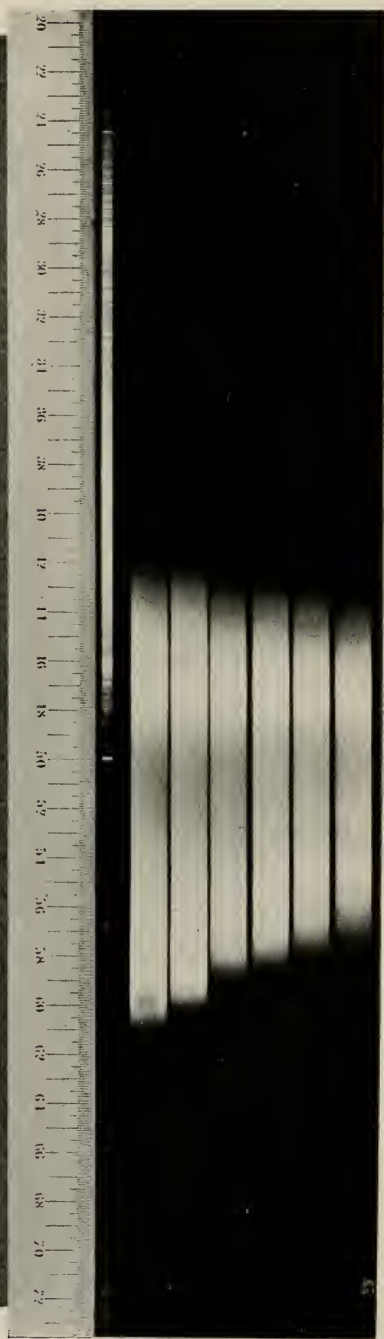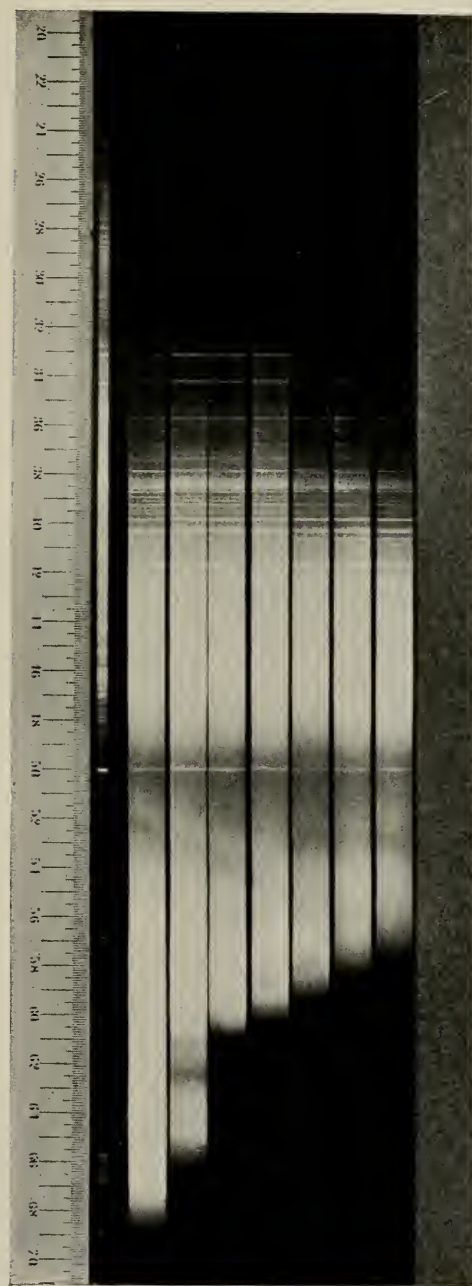
0.125 normal and the depth of cell 8 mm. The time of exposure to the Nernst glower with a current of 0.8 ampere and a slit width of 0.20 mm. was 2 minutes. The length of exposure to the spark was 6 minutes. Starting with the strip adjacent to the comparison spectrum, the temperatures were 6°, 20°, 33°, 47°, 59°, 73° and 80°.

In this spectrogram the effect of temperature on the absorption spectra of cobalt sulphocyanate was very small as compared with the effect on the 2-normal solution. At 6° the ultraviolet band absorbed pretty completely up to λ 3220. There was a slight transmission of light where a strong spark line was located, but this was small. The edge of the band was quite sharp. The yellow-green band extended from λ 4600 to λ 5500. At 80° the ultraviolet band has absorbed everything to λ 3300. The yellow-green band at this temperature runs from λ 4600 to λ 5600, showing a slight widening on the side of the longer wave lengths.

Nickel Acetate.—A spectrogram, Plate XI, A, was made of a 0.5 normal aqueous solution of nickel acetate, the depth of layer being 9 mm. The length of exposure to the Nernst glower was 2 minutes, and to the spark 6 minutes. The current in the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison spark, the temperatures were 6°, 23°, 38°, 52°, 64°, 74° and 84°.

The absorption spectrum of nickel acetate is characterized by a band in the violet and a slight absorption in the ultraviolet. At 6° the absorption in the ultraviolet is very small. At 84° it extends to about λ 2600. At 6° the violet band runs from λ 3800 to λ 4150. There is considerable transmission in this region at the lower temperatures. At the higher temperatures the limits of this band are $\lambda\lambda$ 3700 and 4400.

A spectrogram, Plate XI, B, of a 0.5 N solution of nickel acetate in water was made for various temperatures between 5° and 81°, the depth of layer being 3 mm.

At 5° there is almost complete transmission from λ 2300 to λ 7100. The only effect of rise in temperature was to increase slightly the absorption at the ultraviolet end of the

spectrum and to slightly weaken the transmission in the region λ 4000.

Nickel Sulphate.—A spectrogram was made of the absorption spectra of a 2-normal aqueous solution of nickel sulphate 3 mm. deep. The length of exposure to the Nernst glower was 2 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison spectrum the temperatures were 5°, 19°, 32°, 47°, 61°, 72° and 81°.

Nickel sulphate is remarkable for the fact that it has practically no absorption in the ultraviolet. The violet band at 5° extends from λ 3700 to λ 4200 and at 81° from λ 3700 to λ 4350. It will thus be seen that the effect of temperature upon the absorption spectrum of nickel sulphate is very small and consists simply in the violet band widening slightly in the direction of the red.

Copper Bromide.—The two spectrograms, Plate XII, showing the absorption spectra of copper bromide in water for various temperatures were made for different concentrations of the salt. A gives the absorption of a 2.06 normal solution 1 mm. thick and B the absorption of a 0.25 normal solution 8 mm. thick. The time of exposure to the Nernst glower was 2 minutes (current 0.8 ampere and slit width 0.20 mm.) and to the spark 6 minutes. Starting with the strip nearest the comparison scale, the temperatures at which exposures were made for A were 6°, 17°, 30°, and 45°; for B 6°, 17°, 31°, 46°, 59°, 71° and 85°.

As the spectrograms show, the effect of change in temperature on the absorption spectrum is very marked. Above 45° the concentrated solution did not transmit enough light to affect the photographic film.

Chromium, Calcium and Aluminium Chlorides.—A, Plate XIII, represents a spectrogram showing the effect of rise in temperature on an aqueous solution of chromium and aluminium chlorides. The concentration of the chromium chloride was 0.125 normal, and that of the aluminium chloride 2.28 normal. The depth of layer was 9 mm. The length of

Plate XI.

B.

A.

Plate XII.

Plate XIII.
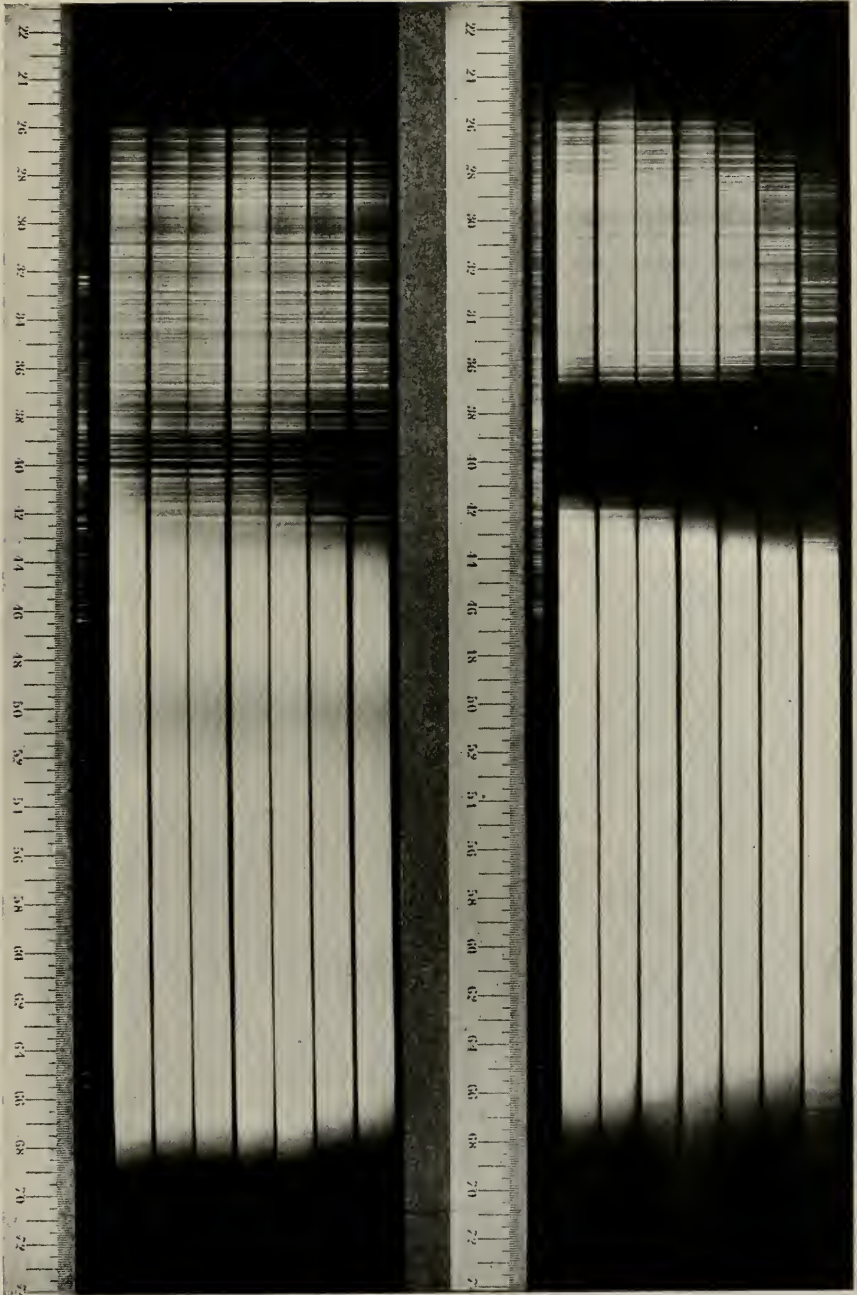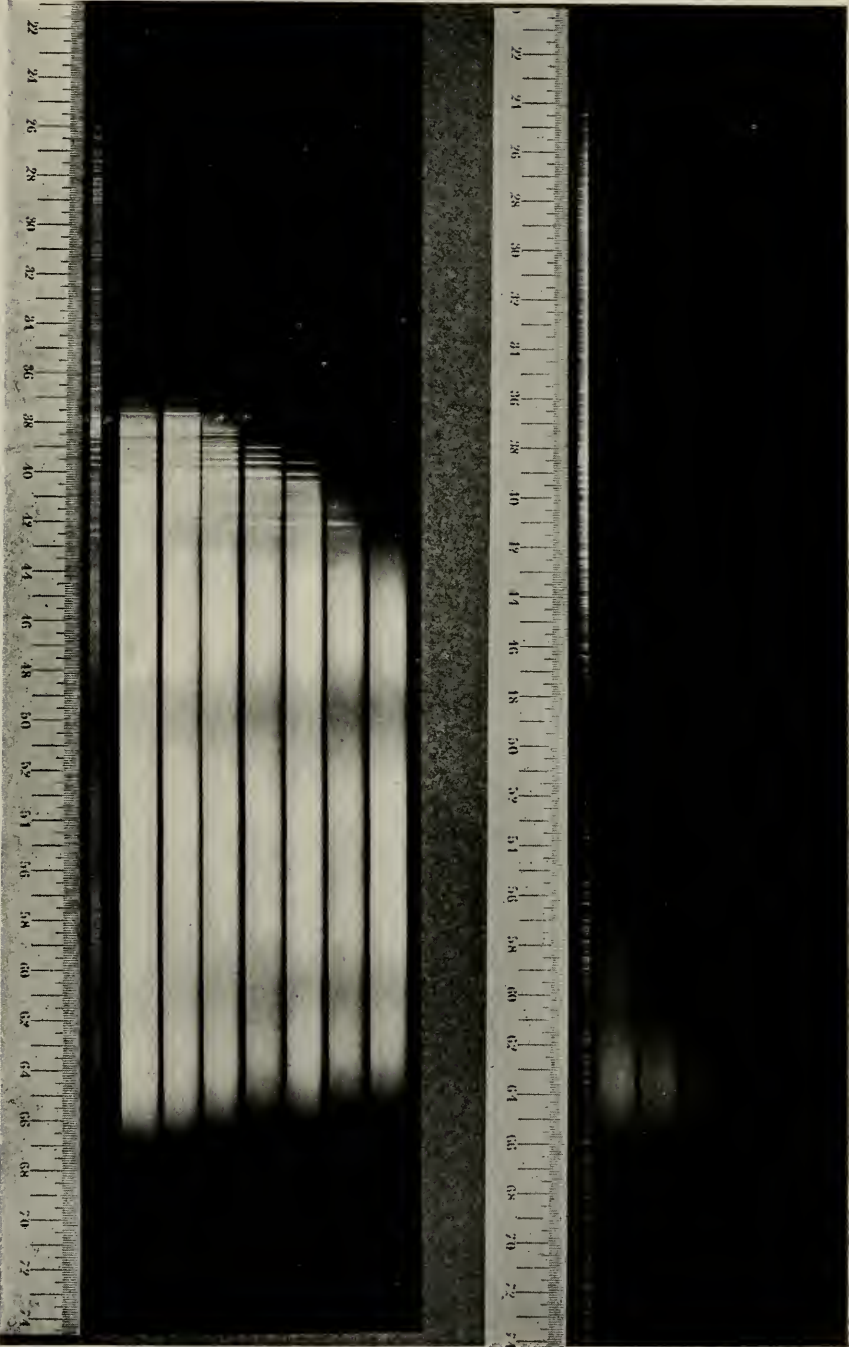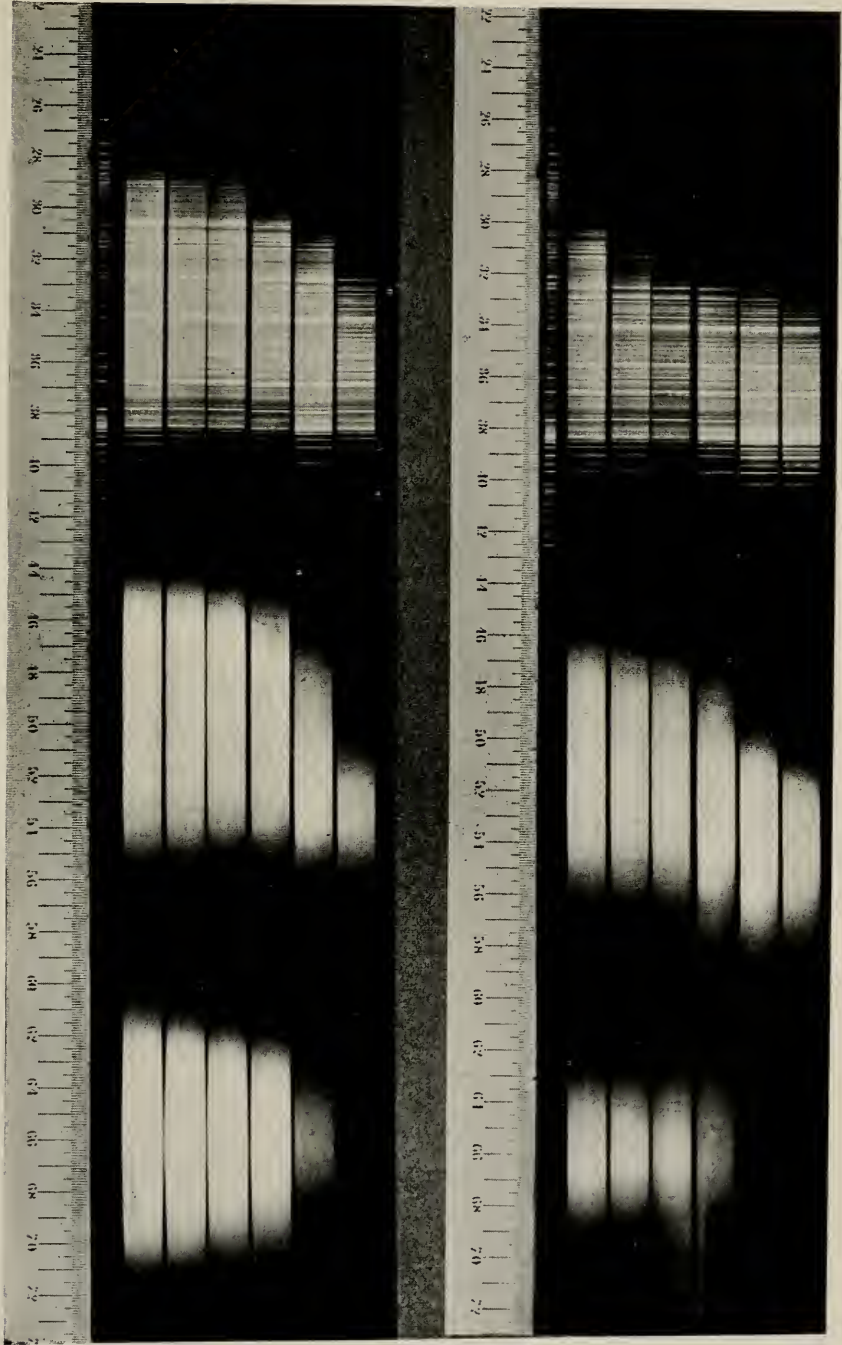
exposure to the Nernst glower was 4 minutes (current 0.8 ampere and slit width 0.20 mm.) and to the spark 6 minutes. Starting with the strip adjacent to the comparison scale, the temperatures were 6°, 19°, 36°, 51°, 66° and 81°.

The most marked effect of the aluminium chloride was the production of a very pronounced unsymmetrical broadening which does not occur when a pure aqueous solution of chromium chloride is heated. At 6° the ultraviolet band extends to λ 3000, at 81° to λ 3300, a much greater widening than takes place for a chromium chloride solution in water. At 6° the blue-violet band extends from λ 4100 to λ 4600 and the yellow band from λ 5800 to λ 6200. Not only do the red sides of the blue-violet and yellow bands widen out enormously towards the red, but the short wave-length edges of these bands actually move towards the red. This effect is much more pronounced in the changes in temperature from 51° to 66° and from 66° to 81°. At 81° the blue-violet band extends from λ 4150 to λ 5050 and the yellow band from λ 5900 throughout the remaining portion of the spectrum, as far as the film is sensitive. The fine chromium bands in the red do not appear.

B, Plate XIII, is a spectrogram giving the absorption spectrum of a 0.125 normal solution of chromium chloride and a 3.45 normal solution of calcium chloride in water at different temperatures. The depth of the solution was 9 mm., the length of the exposures to the Nernst glower 5 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures at which the exposures were made were 6°, 19°, 31°, 45°, 64° and 80°.

The effect of rise in temperature on the absorption spectrum of a mixture of chromium chloride and calcium chloride is very similar to the effect on the mixture of chromium chloride and aluminium chloride. The blue-violet and the yellow bands widen unsymmetrically, and the short wave-length edges of these bands apparently move towards the red at the higher temperatures.

At 6° the ultraviolet band extends to λ 2800, the blue-violet band from λ 4000 to λ 4400 and the yellow band from λ 5600 to λ 6100. At 64° the ultraviolet band extends to λ 3100, the blue-violet band from λ 4000 to λ 4600 and the yellow band from λ 5650 to λ 6300. At 80° the ultraviolet band extends to λ 3250, the blue-violet band from λ 3950 to λ 5000 and the yellow band from λ 5700 throughout the red end of the spectrum as far as the film is sensitive.

Uranyl Chloride.—A spectrogram, A, Plate XIV, was made of the absorption spectrum of a normal aqueous solution of uranyl chloride, the depth of cell being 3 mm. Exposures were made to the Nernst glower for 90 seconds (current 0.8 ampere and slit width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting from the comparison spectrum, the temperatures were 6°, 18°, 34°, 52°, 68° and 82°.

At 8° the ultraviolet band extended to λ 3550, the blue-violet band from λ 4000 to λ 4450. The bands *a*, *b* and *c* appeared, but the *a* band is very faint. The wave lengths of the *b* and *c* bands were $\lambda\lambda$ 4565 and 4725.

At 82° the ultraviolet band extends to λ 3700, and the blue-violet band from λ 3950 to λ 4600. At this temperature only the *b* band appears, *a* being very weak and *c* completely merged into the blue-violet absorption band. The *b* band is located at λ 4755.

A spectrogram, B, Plate XIV, was made of a 0.0156 normal aqueous solution of uranyl chloride 196 mm. deep. Exposures were made to the Nernst glower for 30 seconds (current 0.8 ampere and slit width 0.20 mm.). No exposures were made to the spark except for comparison spectra. Starting with the numbered scale, the temperatures were 6°, 18°, 29°, 44°, 59°, 71° and 79°.

For this concentration there is a very slight temperature effect. There is a very faint transmission band between the ultraviolet and blue-violet bands. This is extremely faint and is practically unaffected by temperature. The blue-violet band widened slightly with rise in temperature. The uranyl bands in the concentrated solution were much stronger and wider than in the dilute solution.

Plate XIV.
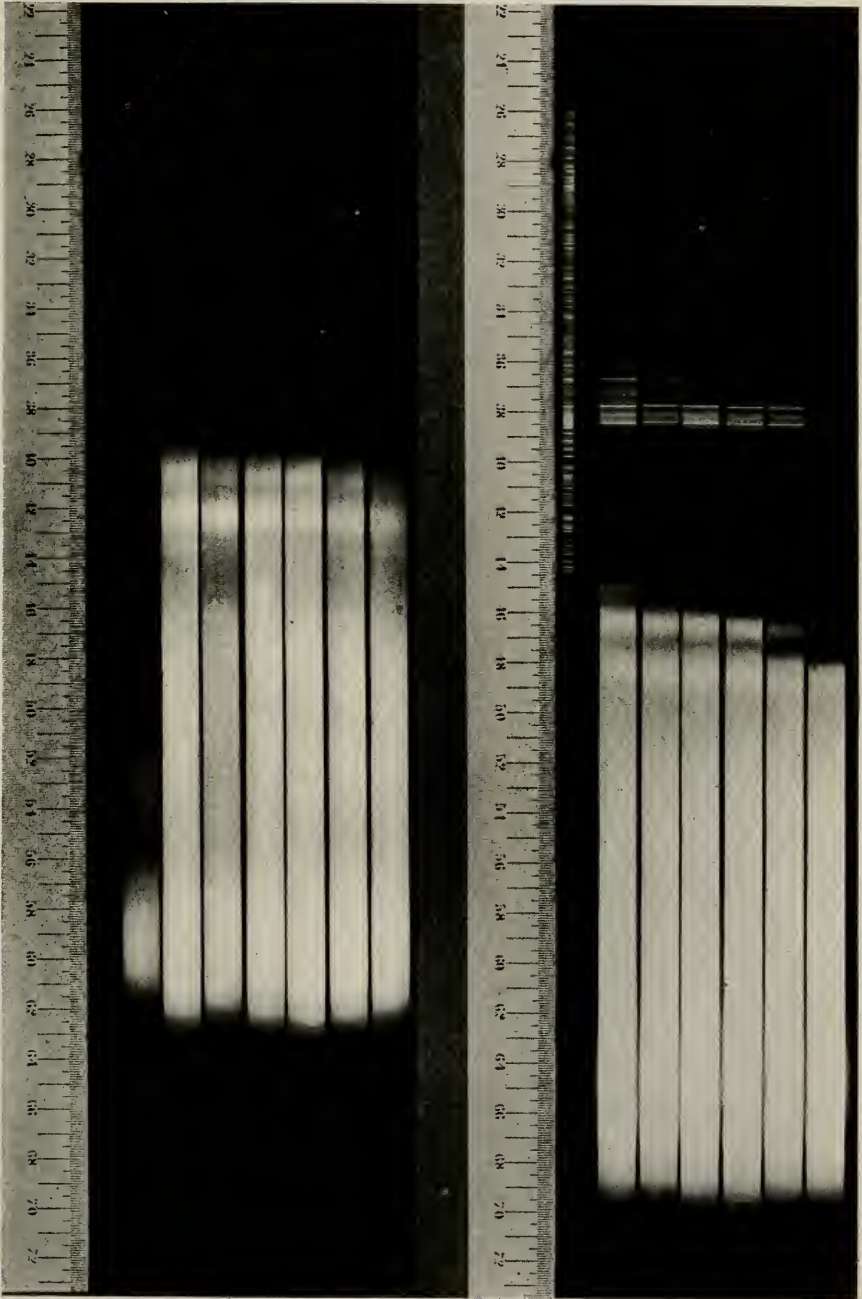
B   A

Uranyl Nitrate.—A spectrogram was made of a 0.0156 normal uranyl nitrate solution in water, the depth of layer being 196 mm. Exposures were made to the Nernst glower for 30 seconds, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the scale, the temperatures were 9°, 23°, 46°, 59°, 70° and 79°.

At 9° the ultraviolet absorption band extended to λ 3430. Throughout the blue-violet band there was considerable transmission at this temperature, the stronger spark lines being only partially absorbed. The *a*, *b* and *c* bands appeared, all being extremely weak, however, and in quite striking contrast with their strength in the aqueous solutions investigated in the earlier part of the work. Their wave lengths were $\lambda\lambda$ 4550, 4705 and 4870.

As the temperature was raised, both the ultraviolet and the blue-violet bands widened. The intensity of the uranyl bands, on the other hand, did not seem to vary with the temperature. At 79° the ultraviolet band extends to λ 3550. The blue-violet band extends from λ 3900 to λ 4450. Only the *a* and *b* bands appear at this temperature, their positions being λ 4710 and λ 4875. There may be a slight shift towards the red, but if there is, it is too small in amount to be established with certainty.

Uranyl Acetate.—A spectrogram showing the effect of rise in temperature was made for a 0.0039 normal aqueous solution of uranyl acetate 196 mm. deep. The exposures were made for 30 seconds to the Nernst glower, with a current of 0.8 ampere and a slit width of 0.20 mm. No exposure was made to the spark at all. The temperatures, starting with the strip nearest the comparison spectrum, were 6°, 18°, 30°, 43°, 56°, 68° and 75°.

The spectrogram shows the ultraviolet and blue-violet bands common to all uranyl salts. The transmission band between these absorption bands is about 200 A. U. wide and changes very little with change in temperature. The blue-violet band advances rapidly towards the red as the temperature rises. At 6° the blue-violet band extends from λ 3950

to λ 4500. The latter edge gradually runs towards the red until at 75° it is about λ 4600. The uranyl bands *a* and *b* appear. These are very weak and gradually shift towards the red with rise in temperature.

Uranous Chloride.—To a normal solution of uranyl chloride in water was added a small amount of hydrochloric acid and zinc. The production of hydrogen reduced the uranyl to the uranous state. The same can be done in some cases by simply passing hydrogen gas through the uranyl solution. The solution was placed in the glass trough and a temperature run made as in the usual manner. The thickness of layer was 1 mm. The length of exposure was 50 seconds to the Nernst glower and 4 minutes to the spark, the current through the glower being 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison scale, the temperatures were 8°, 17°, 33°, 48°, 62° and 73°. An exposure was also made at 80° which is not shown in the spectrogram B.

At 8° a mist formed on the prisms and for this reason the spectrum film taken at this temperature is much underexposed and the bands appear wider than at the higher temperatures. At this temperature there is complete absorption of the shorter wave lengths to λ 3650. A blue-violet absorption extends between λ 4050 and λ 4450. Following this band are three strong bands of about equal intensity and each almost 100 A. U. wide. Their wave lengths are approximately $\lambda\lambda$ 4590, 4760 and 4970. Following is a band at λ 5500, a wide band from λ 6400 to λ 6630 and a rather narrow band at λ 6740.

The absorption does not change very greatly until a temperature of 60° is reached. About this temperature the increase in absorption is quite rapid as the temperature rises. At 73° the ultraviolet band has widened to λ 3800, the blue-violet band covers the region from λ 4050 to λ 5000. The bands $\lambda\lambda$ 4600, 4770 and 4980 at 8° have shifted slightly to the red with rise in temperature.

None of the other bands seem to shift to the red at all and the broadening seems to be quite symmetrical. The band at λ 5500 has become about twice as wide as it was at the

lower temperatures, and the two red bands have merged into one band running from $\lambda\,6350$ to $\lambda\,6800$. Between 73° and 80° the absorption increases very greatly. All short wave lengths are absorbed up to $\lambda\,5050$. The band in the green runs from $\lambda\,5450$ to $\lambda\,5600$ and the band in the red has also widened very greatly, extending from $\lambda\,6200$ to $\lambda\,6800$.

Uranyl Sulphate.—A spectrogram was made for a normal solution of uranyl sulphate, the depth of cell being 3 mm. The time of exposure was 90 seconds to the Nernst glower with a current of 0.8 ampere and a slit width of 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest the numbered scale, the temperatures were 5°, 19°, 32°, 54°, 67° and 84°.

The rise in temperature from 5° to 84° caused an encroachment of the ultraviolet band into the regions of greater wave length. The blue-violet band increased in width, especially towards the red, as the temperature was raised. The uranyl bands themselves changed very slightly in intensity with rise in temperature.

At 5° the ultraviolet was absorbed to $\lambda\,3500$. The blue-violet band extended from $\lambda\,3900$ to $\lambda\,4400$. The uranyl bands a, b and c appeared at $\lambda\lambda\,4570$, 4730 and 4910.

At 84° the ultraviolet band extended to $\lambda\,3600$, the blue-violet band from $\lambda\,3850$ to $\lambda\,4550$. The bands a, b and c have become considerably more diffuse. Their positions are $\lambda\lambda\,4590$, 4745 and 4925, approximately.

Uranyl Sulphate.—A much more dilute solution (0.0156 normal) of uranyl sulphate (Plate XV, B), containing approximately the same amount of salt as the concentrated solution, was used. The length of cell in this case was 196 mm. The exposure was for 30 seconds to the Nernst glower (current 0.8 ampere, slit width 0.20 mm.). The time of exposure to the spark was 4 minutes. Starting with the strip next the comparison scale, the temperatures were 6°, 19°, 36°, 51°, 67° and 81°.

At 6° the ultraviolet band extends to $\lambda\,3500$, and the blue-violet band from $\lambda\,3950$ to $\lambda\,4450$. The positions of the a, b and c bands are $\lambda\lambda\,4565$, 4720 and 4895. At 81° the ultra-

violet absorption extended to $\lambda\,3600$ and the blue-violet band from $\lambda\,3900$ to $\lambda\,4500$. The a and b bands were located at $\lambda\lambda\,4735$ and 4915. The effect of concentration upon the temperature coefficient seems to be very small. In both concentrations, as the temperature was increased there was a slight shift of the uranyl bands to the red.

Praseodymium Chloride.—A spectrogram, Plate XVI, A, was made of a 2.56 normal aqueous solution of praseodymium chloride 3 mm. deep. Exposures were made to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) for 20 seconds. The time of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 7°, 23°, 40°, 52°, 68° and 84°.

The ultraviolet is absorbed up to $\lambda\,2700$ and this absorption does not vary greatly with temperature, increasing slightly, however. At 7° there are bands from $\lambda\,4385$ to $\lambda\,4500$, $\lambda\,4640$ to $\lambda\,4720$, $\lambda\,4810$ to $\lambda\,4845$, $\lambda\,6860$ to $\lambda\,6990$. This latter band is double, the red component being much the narrower and having its center at $\lambda\,6980$. Throughout the remainder of the spectrum there is complete transmission.

At 84° the absorption bands are located at $\lambda\lambda\,4380$ and 4510, $\lambda\lambda\,4640$ and 4730, $\lambda\lambda\,4810$ and 4845, and $\lambda\lambda\,6870$ and 6775. The bands all widen slightly except the latter. At 7° the latter band consisted of two separate bands. At 84° the $\lambda\,6980$ band has diffused into the other band and the general transmission throughout the band has been greatly increased. In this respect this band is very peculiar indeed, and behaves with respect to temperature changes in just the opposite way from practically all other bands investigated.

Praseodymium Chloride.—A spectrogram, Plate XVI, B, was made of a 0.043 normal aqueous solution of praseodymium chloride 196 mm. deep. This spectrogram was to show whether changes due to temperature in the spectrogram were affected by the concentration of the solution. The length of exposure to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) was 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest

Plate XV.

B   A

Plate XVI.
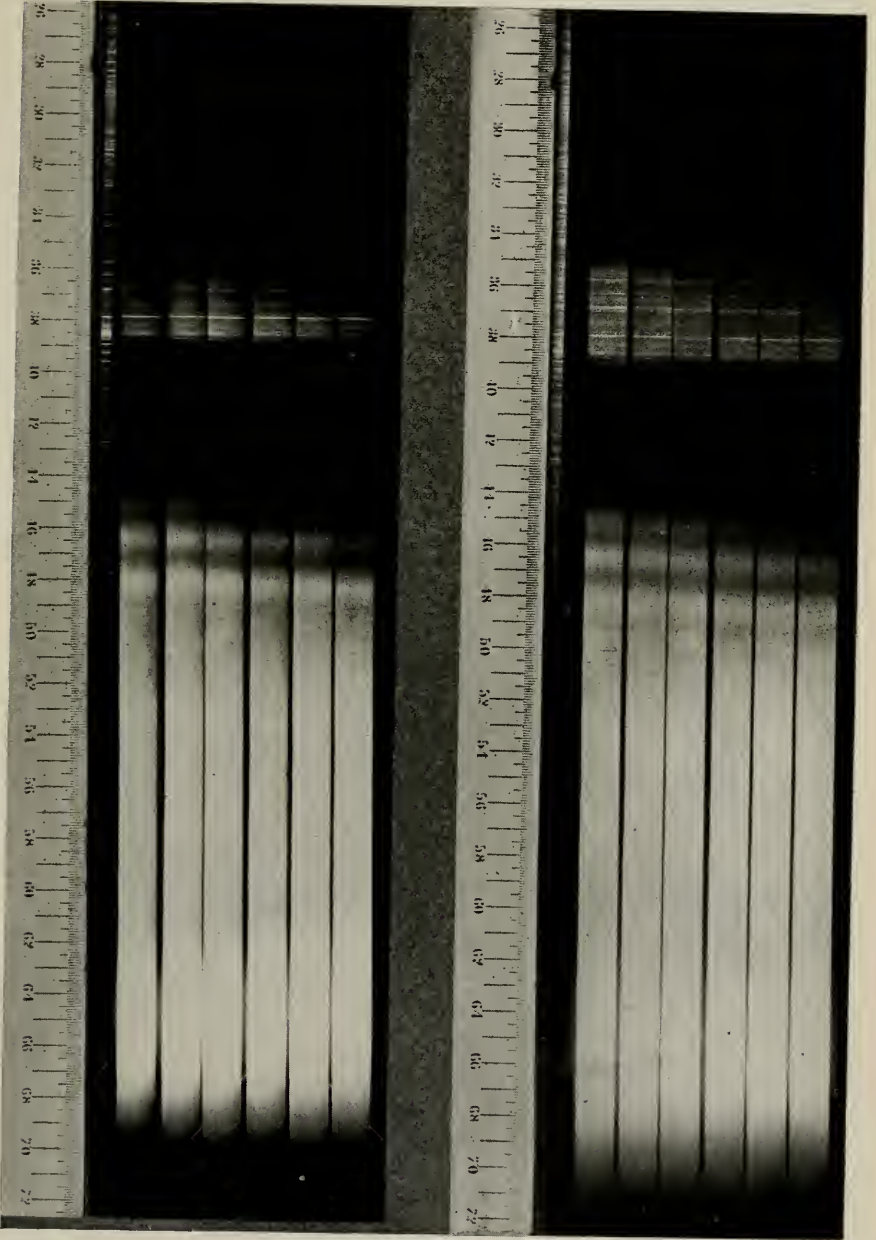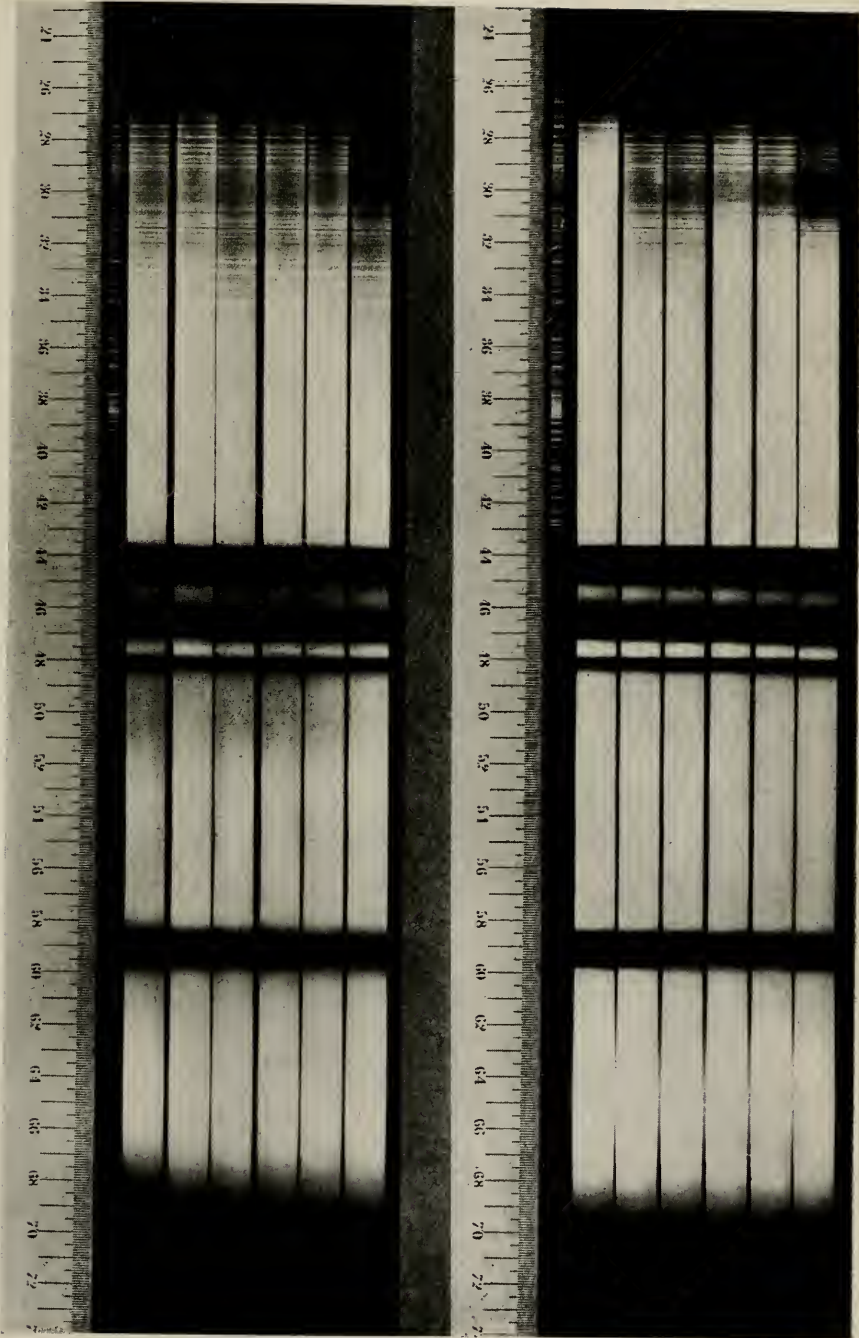
the comparison spectrum, the temperatures were 7°, 20°, 36°, 51°, 66° and 82°

The absorption spectrum of the dilute solution is practically the same as that for the concentrated solution. At 7° bands occur from λ 4385 to λ 4490, λ 4640 to λ 4715, λ 4810 to λ 4840, λ 5860 to λ 5940 and a narrower band at λ 5980.

The ultraviolet absorption at 7° extends to λ 2650, at 82° it extends to λ 2750. The other bands are at $\lambda\lambda$ 4385, 4490, $\lambda\lambda$ 4650, 4715, $\lambda\lambda$ 4805 to 4835, $\lambda\lambda$ 5870 to 5930. The band λ 5980 has become much more diffuse. The band adjacent to it has also become narrower and much more filled up by general transmission than at the lower temperatures. It will be seen in general that there is very little, if any, temperature change in the absorption bands of praseodymium chloride at this concentration, except the bands in the red, which become narrower and weaker at the higher temperatures. In the concentrated solution the change in this band was not as great as in the dilute solution. In the concentrated solutions the other bands widened slightly more than they do in the solution here described.

Praseodymium Nitrate.—A spectrogram, Plate XVII, A, showing the effect of rise in temperature was made for a 2.6 normal aqueous solution of praseodymium nitrate 46.5 mm. deep. The exposures were made to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) for 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the comparison scale, the temperatures were 6°, 19°, 47°, 70° and 90°.

On account of the great concentration and the depth of cell, the absorption bands are very wide. The whole ultraviolet portion of the spectrum is absorbed up to λ 3550. Rise in temperature does not cause any change in this absorption. The band in the blue extends from λ 4300 to λ 4940 at 6°. A weak and rather broad band appears at λ 5120 and a narrow band at λ 5240, this band being about 15 A. U. wide. The yellow band extends from λ 5760 to λ 6120 at 6°.

As the temperature rises the blue and yellow bands gradually widen. At 47° the blue band extends from λ 4290 to

λ 4950, the yellow band from λ 5750 to λ 6120. At 90° the violet band was bounded by $\lambda\lambda$ 4280 and 4960, the yellow band by $\lambda\lambda$ 5740 and 6140. At 70° the ballast burned and the exposure to the Nernst glower was not quite as long as it should have been.

The bands $\lambda\lambda$ 5120 and 5240 appeared very slightly affected by the rise in temperature here used. The violet and yellow bands broadened very slightly with rise in temperature and broadened symmetrically.

Plate XVIII, A, represents the absorption spectra of a 2.6 normal solution of praseodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures are 6°, 16°, 34°, 46°, 58°, 70° and 82° C.

The four characteristic wide absorption bands appear very slightly affected by rise in temperature. The NO_3 band in the ultraviolet widens slightly.

Praseodymium Chloride.—This spectrogram, Plate XVIII, B, of an aqueous solution of praseodymium chloride shows the effect of change of temperature between 7° and 84° on a 2.56 normal solution 48.00 mm. deep. The exposure to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) was for 20 seconds. The exposure to the spark was for 4 minutes. Starting from the comparison spectrum, the strips were taken at the temperatures 7°, 20°, 35°, 51°, 66° and 84°.

The spectrum strip taken at 7° shows a large band in the blue and one in the yellow. There is absorption in the ultraviolet. In the case of praseodymium nitrate the absorption in the ultraviolet was probably due to the NO_3 band. This absorption was found to be unaffected by temperature. In the case of praseodymium chloride the absorption increases very markedly with rise in temperature. At 7° the limits of the blue band are $\lambda\lambda \begin{Bmatrix} 4280 \\ 4270 \end{Bmatrix}$ and $\begin{Bmatrix} 4940 \\ 4930 \end{Bmatrix}$ and for the yellow band $\lambda\lambda$ 5750 and 6100. There is slight absorption in the region λ 5000 to λ 5100, which is probably due to absorption bands. Two fine bands, each about 8 A. U. wide, appear at $\lambda\lambda$ 5220 and 5235. Absorption of the shorter wave lengths

Plate XVII.

B

A

Plate XVIII.

B

A
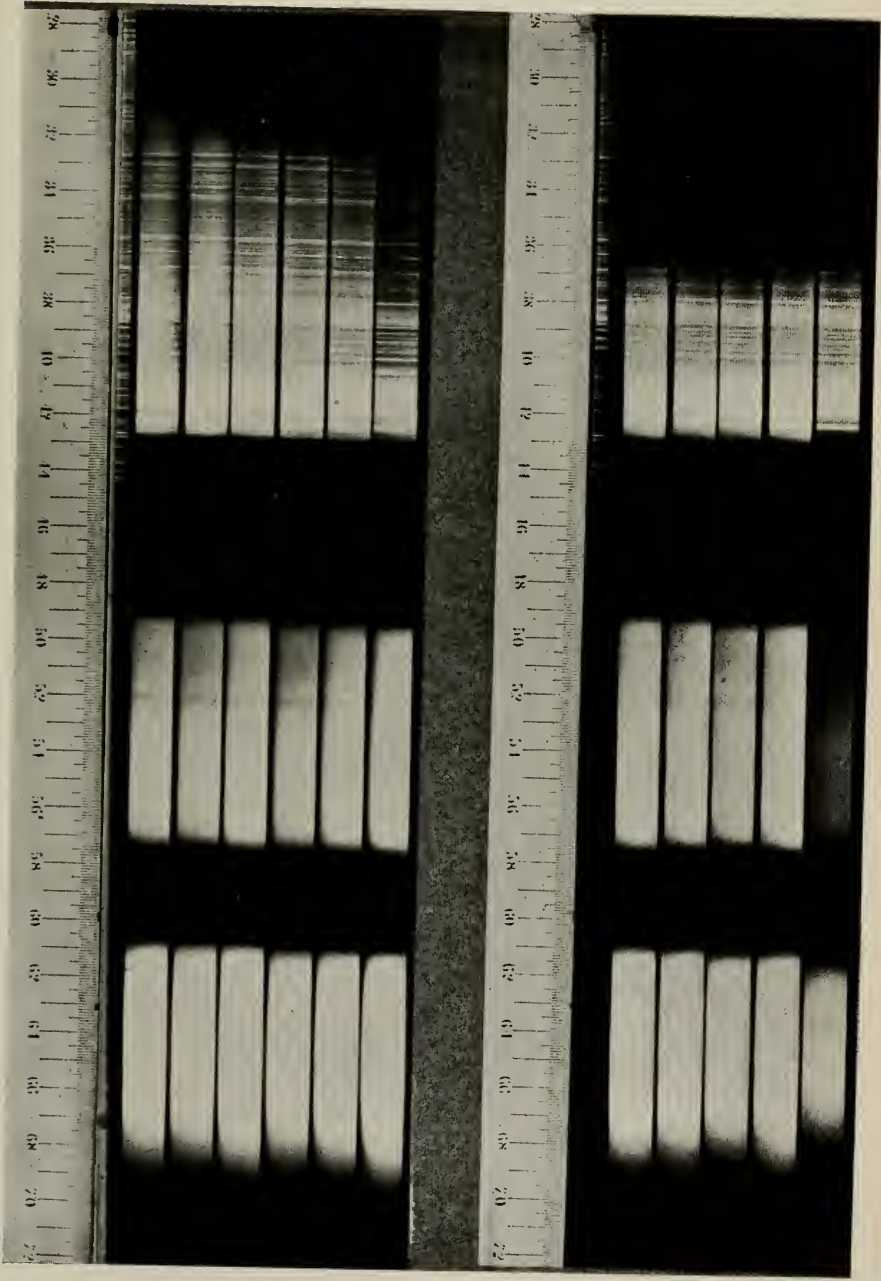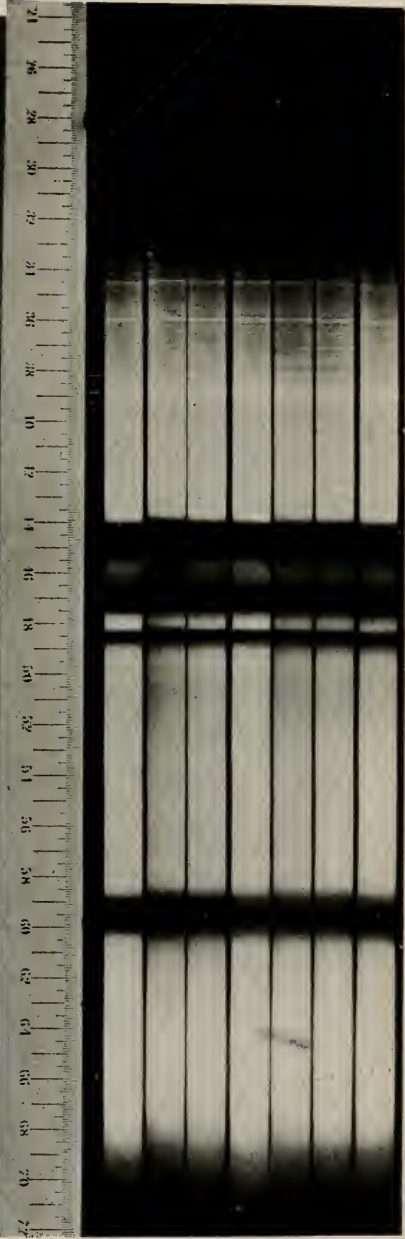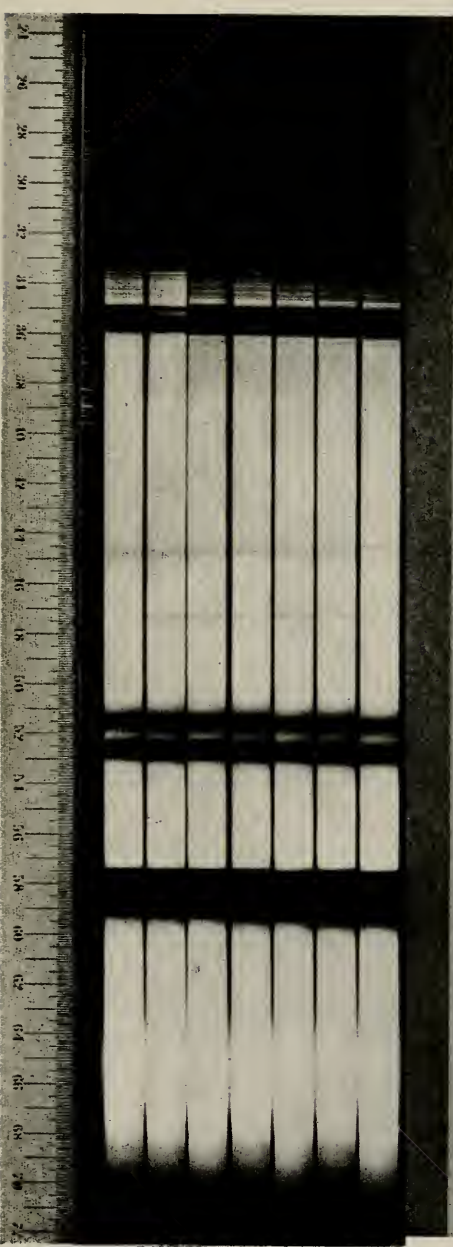
at 7° is complete to λ 3100, at 51° λ 3200, and at 84° λ 3300. At 51° the blue band is located at $\lambda\lambda$ 4280 and 4950, and the yellow band at $\lambda\lambda$ 5740 and 6110.

At 84° the limits of the blue band are $\lambda\lambda$ 4280 and 4950, and of the yellow band $\lambda\lambda$ 5750 and 6110. The widening of the bands is very small indeed. The fine bands $\lambda\lambda$ 5220 and 5235 become much more diffuse and at the higher temperatures could not be resolved at all. At 7°, however, the two bands were entirely separated. The blue and yellow bands are very slightly affected by temperature within the ranges investigated.

Neodymium Chloride.—A spectrogram, Plate XX, A, of a 3.4 normal solution of neodymium chloride in water, 43 mm. deep, was taken. The exposures were made for 3 minutes to the Nernst glower, the current being 0.8 ampere and slit width 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison spark, the temperatures were 6°, 21°, 36°, 47°, 60°, 77° and 83°.

Neodymium chloride, under the conditions of this experiment, gives a complete absorption in the ultraviolet up to λ 3700. From λ 3700 throughout the violet and blue regions there is almost complete general absorption, this general absorption increasing with the temperature. A band of absorption seems to appear at about λ 4000, but this is somewhat doubtful. A very sharp and strong band appears at λ 4185. A band occurs at $\lambda\lambda$ 4265, 4305 and one at $\lambda\lambda$ 4320 and 4350. The transmission band between these two bands is faint and disappears at 77°. An absorption band extends from λ 4380 to λ 4520 and there is then complete absorption up to λ 4980. The transmission between these bands is very weak and has almost disappeared at 83°. Between $\lambda\lambda$ 4970 and 5365 there is an absorption band, the long wave-length edge of this band being extremely sharp. A similar band lies between $\lambda\lambda$ 5620 and 6000. Next comes a series of five absorption bands. The first of these is 20 A. U. wide and is at λ 6250, the next is 10 A. U. wide and is at λ 6270. The bands $\lambda\lambda$ 6295 and 6315 almost touch each other, the distance between them being

but two or three A. U. The last band is about 30 A. U. in width and its center lies at $\lambda\,6380$. The last band that could be photographed was between $\lambda\,6720$ and $\lambda\,6965$.

The effect of rise in temperature is quite evident, most of the bands widening and their sharpness gradually decreasing. At 83° the band $\lambda\lambda\,4970$–5365 described above has widened to $\lambda\lambda\,4960$ and 5395, the widening being slightly greater on the red side. The band $\lambda\lambda\,5620$ to 6000 has widened to $\lambda\lambda\,5610$ and 6050, this widening also being unsymmetrical. The five bands in the vicinity of $\lambda\,5800$ at 6° have merged into three bands. The red band is at $\lambda\lambda\,6720$ to 6990. It will thus be seen that the widening is in general greater on the red side of the bands.

Neodymium Nitrate.—A spectrogram, Plate XX, B, was made of a 2.96 normal aqueous solution of neodymium nitrate 38.5 cm. deep. An exposure of 3 minutes was made to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale the temperatures were 7°, 17°, 30°, 44°, 59°, 70° and 82°.

At 7° there is practically complete absorption in the ultraviolet up to $\lambda\,4600$, due to the absorption of the NO_3 group. The edge of the band is very sharp. Other bands are as follows: $\lambda\,4270$ to $\lambda\,4288$, $\lambda\,4386$ to $\lambda\,4500$, $\lambda\,4538$ to $\lambda\,4870$, $\lambda\,4970$ to $\lambda\,5370$, $\lambda\,5620$ to $\lambda\,6005$, $\lambda\,6240$ to $\lambda\,6270$, and $\lambda\,6705$ to $\lambda\,6970$.

It should be noticed here that the absorption spectrum of neodymium nitrate under the present conditions is quite different from the absorption of a similar solution of neodymium chloride. In the case of the chloride there was a very great amount of absorption throughout the ultraviolet and violet portions of the spectrum. In the case of the nitrate there is almost complete absorption up to $\lambda\,3600$ and from that wave length to $\lambda\,4270$ there is complete transmission. In this region appeared several narrow and sharp bands in the neodymium chloride absorption spectrum.

From the spectrum shown in the upper strip and for which

Plate XIX.

B   A

Plate XX.

B

A
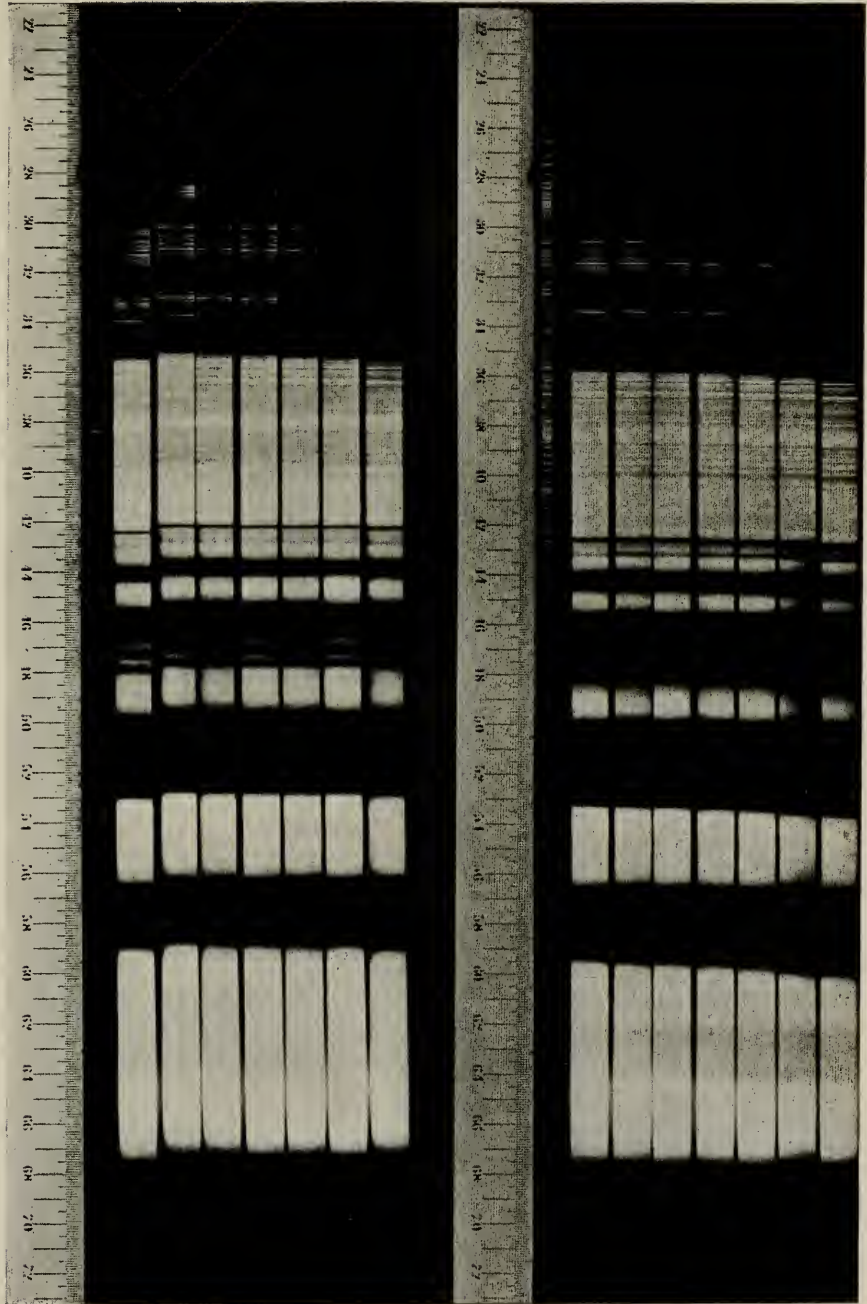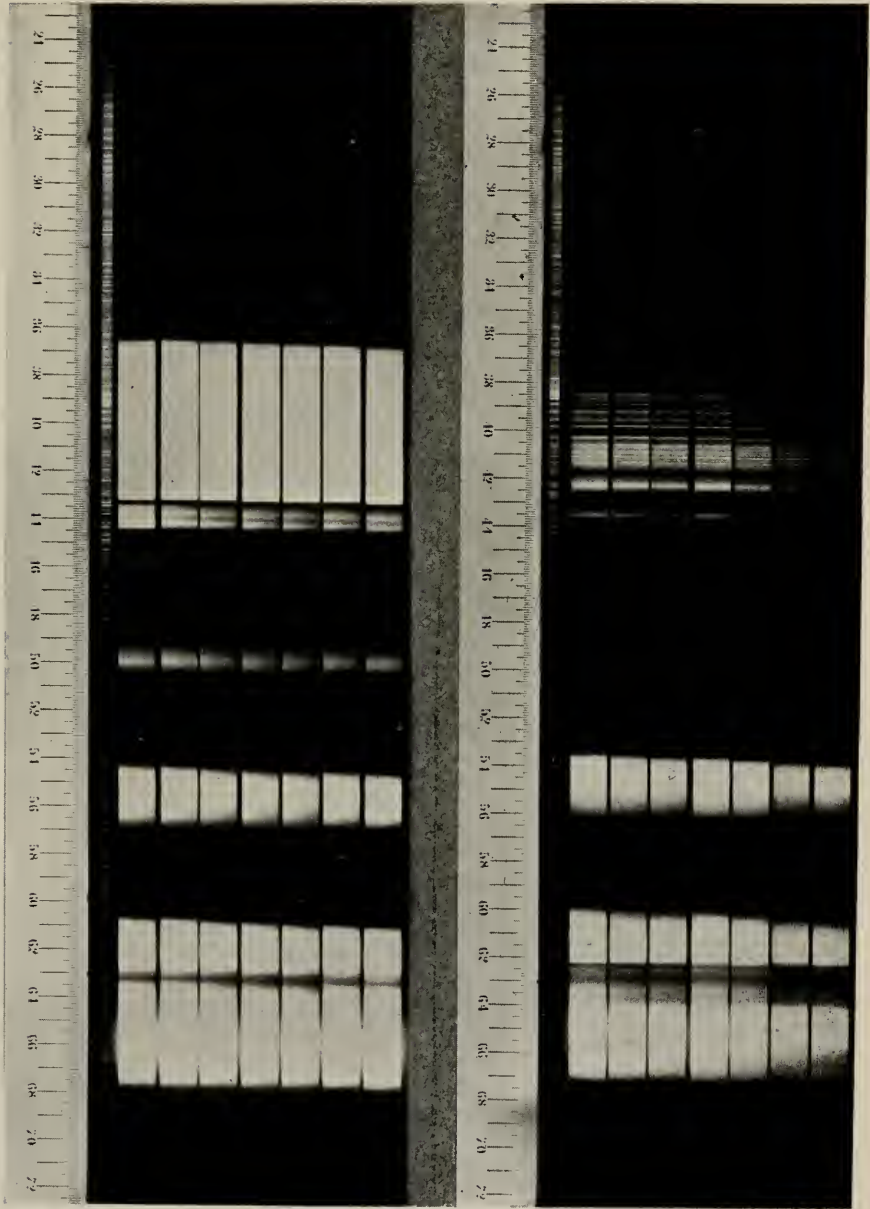
the temperature was 82° we see that the NO_3 band extends to $\lambda\,3615$. The band $\lambda\,4274$ has become about 5 A. U. wider than it was at 7°. A wide and weak band appears at $\lambda\,4350$ and this is considerably stronger than at the lower temperatures. The positions of the other bands are: $\lambda\,4380$ to $\lambda\,4560$, $\lambda\,4535$ to $\lambda\,4870$, $\lambda\,4970$ to $\lambda\,5390$, $\lambda\,5615$ to $\lambda\,6025$ and $\lambda\,6700$ to $\lambda\,6970$. The increase in width of these bands due to increasing the temperature from 7° to 82°, is 60, 20, 25 and about 0 A. U., respectively.

Plate XVIII, B, represents the absorption spectra of a 2.15 normal solution of neodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures were 4°, 17°, 29°, 44°, 58°, 71° and 84°.

As the temperature rises the NO_3 band widens slightly. The bands in the region of $\lambda\,3500$ become more diffuse and slightly wider. The same is true of the bands at $\lambda\,5200$. The broad band at $\lambda\,5800$ widens, especially on the long wavelength edge.

Neodymium Salts.—A spectrogram, A, Plate XIX, of the absorption spectrum as affected by change in temperature was made for a neodymium chloride solution in water, the concentration being 3.4 normal and the depth of layer 12 mm. The length of exposure was 2 minutes to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting with the strip nearest the numbered scale, the temperatures were 11°, 22°, 33°, 45°, 59°, 73° and 85°.

At 11° an absorption band appears at about $\lambda\,2970$, a very strong band from $\lambda\,3250$ to $\lambda\,3285$, and an adjacent band from $\lambda\,3285$ to $\lambda\,3310$. A very narrow and feeble transmission band separates these two bands. At 85° the transmission band has weakened very much. At 11° a very strong band lies between $\lambda\,3490$ and $\lambda\,3580$. The band $\lambda\,4274$ is about 8 A. U. wide. An extremely narrow band appears at $\lambda\,4297$, $\lambda\,4306$ and $\lambda\,4324$. At $\lambda\,4234$ is a wider and rather diffuse band, it being about 12 A. U. wide. Bands lie between $\lambda\lambda\,4415$ and 4470, $\lambda\lambda\,4580$ and 4650, $\lambda\lambda\,4665$ and 4710, $\lambda\lambda\,4740$ and 4775, $\lambda\lambda\,4815$ and 4835, and the very wide bands $\lambda\lambda\,5010$

and 5300 and $\lambda\lambda$ 5665 and 5935. Weak bands are located at λ 4645, λ 4800, λ 5320, λ 6235, λ 6255, λ 6280, λ 6305 and λ 6380. Rather diffuse bands appear at $\lambda\lambda$ 6780 and 6840, at λ 6850 and from λ 6870 to λ 6920.

The effect of rise in temperature from 11° to 85° is quite noticeable, although it is not great. In the ultraviolet there is a slight increase in the general absorption. The band $\lambda\lambda$ 3285 and 3310 widens slightly. The band $\lambda\lambda$ 3490–3580 at 11° has widened so that at 85° it extends from λ 3450 to λ 3600. The band at $\lambda\lambda$ 4415 and 4470 has widened but little. The bands from λ 4600 to λ 4800 have also widened but little. The faint diffuse bands $\lambda\lambda$ 4645 and 4800 have practically disappeared. The bands $\lambda\lambda$ 5010 and 5300 and $\lambda\lambda$ 5665 and 5935, at 11°, have widened at 85° to $\lambda\lambda$ 5010 and 5350 and $\lambda\lambda$ 5660 and 5985. The widening of the latter band is distinctly unsymmetrical. The existence of the band λ 5320 causes the band λ 5010 to λ 5300 to widen unsymmetrically.

The bands in the region λ 6300 become less sharp as the temperature rises. At 11° there was considerable transmission in the region λ 6850. At 85°, however, this transmission disappears and there is practically complete absorption from λ 6760 to λ 6920. The very sharp bands $\lambda\lambda$ 4282, 4300, 4310, 4322 and 4343 do not appear to change very much with change in temperature. On the strip taken at 73° these bands appear sharper than on any of the other strips.

A spectrogram, B, Plate XIX, showing the effect of rise in temperature was made on a 0.17 normal neodymium chloride solution in water 196 mm. deep. The amount of neodymium chloride in the path of the light is approximately the same as in the spectrogram showing the effect of temperature on a 3.4 normal solution in a cell 12 mm. deep. In this case the temperatures were 5°, 16°, 28°, 42°, 59°, 72° and 82°. Exposures were made to the Nernst glower for 3 minutes (current 0.8 ampere and slit width 0.20 mm.). Each strip was exposed to the spark for 6 minutes. The purpose of making this spectrogram was to find the effect of concentration of a salt upon the changes produced by change in temperature.

A description of the bands at 5° and 82° will be given. Any change that takes place between these two temperatures is a gradual one. Transmission begins at λ 2600. Bands appear between $\lambda\lambda$ 3250 and 3300 and $\lambda\lambda$ 3455 and 3575. The band λ 4274 is much sharper and narrower than for the more concentrated solution. The numerous fine bands in the region λ 4300 are very faint. The bands $\lambda\lambda$ 4420 to 4460, $\lambda\lambda$ 4600 to 4630, λ 4645, $\lambda\lambda$ 4680 to 4705, $\lambda\lambda$ 4745 to 4770 and λ 4820 have rather diffuse edges. Wide bands appear from λ 5020 to λ 5290 and from λ 5685 to λ 5920. Diffuse bands are located at λ 5310, λ 6810 and λ 6900. The group in the region λ 6300 appears, but the bands are extremely faint.

At 82° the general absorption has increased in the ultraviolet and has reached to about λ 2800. It will be noticed here that the effect of rise in temperature upon this general ultraviolet absorption is greater for the dilute solution than for the concentrated solution previously described.

The band $\lambda\lambda$ 3455 to 3575 at 5° has widened slightly, having the limits $\lambda\lambda$ 3445 and 3580 at 82°, the widening being about 15 A. U. This band in the concentrated solution widened 60 A. U. Practically no effect on the bands from λ 4200 to λ 4900 is to be noticed with rise in temperature. At the higher temperature the bands are slightly more diffuse, but this change is very small. The band $\lambda\lambda$ 5020 to 5290 at 5° has widened to $\lambda\lambda$ 5015 and 5285, about 10 A. U. The corresponding widening for the concentrated solution was approximately 50 A. U., although it must be noted that in the more concentrated solution this widening was mostly due to the increased absorption of the band λ 5310 at the higher temperatures. The band λ 5685 to λ 5920 at 5° has widened to $\lambda\lambda$ 5775 and 5930, about 20 A. U., compared with a widening of 55 A. U. for the more concentrated solutions. None of the other bands show any appreciable change with change in temperature.

A spectrogram, A, Plate XXII, was made showing the effect of temperature on the absorption spectrum of a 1.66 normal aqueous solution of neodymium bromide, the depth of layer being 6 mm. An exposure of 4 minutes was made

to the Nernst glower (0.8 ampere and a slit width of 0.20 mm.). The length of exposure to the spark was 6 minutes. The temperatures, starting with the strip adjacent to the comparison spark, were 4°, 20°, 36°, 50°, 68° and 83°.

At 4° there is complete absorption in the ultraviolet up to λ 2600. A broad absorption band appears at λ 2660 to λ 2800 and from λ 2950 to λ 3060. These absorption bands appear with a more or less general absorption. Bands appear at $\lambda\lambda$ 3460, 3500 and 3540. The band at λ 4274 is weak. Weak and diffuse bands occur at $\lambda\lambda$ 4440, 4630, 4695, 4760, 4825, 5095, 5260, 6810 and 6900. Wider bands are located at $\lambda\lambda$ 5116 to 5140, $\lambda\lambda$ 5200 to 5240 and $\lambda\lambda$ 5710 to 5850.

At 83° the spectrum is almost exactly the same as at 4°. The ultraviolet absorption is complete up to λ 3050. The bands at λ 3500 have increased in width slightly and the band λ 4274 is slightly broader. The bands that have widened appreciably are $\lambda\lambda$ 5195 to 5260 and $\lambda\lambda$ 5700 to 5880. The change in the absorption is greater when the temperature is changed from 68° to 83°. Up to 68° there is practically no change in the absorption spectrum at all.

A spectrogram, B, Plate XXII, showing the effect of temperature was made, using a 0.055 normal aqueous solution of neodymium bromide, the depth of the layer being 197.4 mm. This spectrogram was made for comparison with that for a 1.66 normal solution of the same salt 6 mm. deep. The exposures to the Nernst glower lasted 90 seconds in this case (current 0.8 ampere and slit width 0.20 mm). The length of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison scale, the temperatures of the solution were 5°, 16°, 29°, 42°, 55°, 68° and 84°.

At 5° there is practically complete transmission of light between λ 3400 and λ 2600, no ultraviolet bands appearing, as was the case for the more concentrated solution. The bands $\lambda\lambda$ 4445, 4693, 4760, 4825 and 5095 were somewhat sharper than they were in the concentrated solutions. The two largest bands extended from λ 5200 to λ 5250 and from λ 5710 to λ 5850. As in the case of the more concentrated solution, so here, the greatest change in the absorption took place in

Plate XXI.

Plate XXII.

B   A

the change from 68° to 84°. The ultraviolet absorption increased up to λ 2900. The bands at λ 3500 became considerably stronger, but they widened very little. The bands $\lambda\lambda$ 4445, 4693, 4760 and 4825 are somewhat weaker than at 5°. The wide bands remained practically as wide as at 5°, λ 5200 to λ 5250 and λ 5705 to λ 5870. This indicates a widening of about 25 A. U. for the latter band. For the more concentrated solution the widening of these two bands was 25 and 40 A. U., respectively. It is thus seen that in the more concentrated solutions the bands widen more with rise in temperature than they do in the less concentrated solutions. At 42° in the dilute solution there appears a narrow band at λ 6710. This increases in intensity with rise in temperature. This band does not appear at all in the concentrated solution.

A spectrogram, A, Plate XXI, was made of neodymium chloride and calcium chloride in water. Exposures were made for 30 seconds to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 6°, 17°, 31°, 49°, 63°, 74° and 82°.

The general effect of the addition of calcium chloride is to make all the bands hazier, and to increase the transmission throughout the region of the band. At 6° there is a slight transmission throughout the ultraviolet portion of the spectrum. As the temperature is raised this general transmission is decreased, and at 82° practically no light of shorter wave length than λ 2800 passes through the solution. Sharp bands occur at λ 3464, λ 3500, λ 3535, λ 4276 and weak diffuse bands at λ 4295, λ 4305, λ 4340, λ 4445, λ 4620, λ 4695, λ 4760, λ 4825, λ 5095, λ 5130, λ 5225, λ 5260, λ 5320, λ 5710 to λ 5860, λ 6245, λ 6810 and λ 6900.

At 82° the bands in the λ 3500 region are slightly more intense than at 6°. Practically all the bands from λ 4200 to λ 5200 have become much weaker at the higher temperature. This is especially true of the band λ 4276, its intensity being less than half what it is at 6°. Most of the bands are shifted

to the red with reference to the same bands at 6°. For instance, λ 5095 is shifted 5 A. U. towards the red. The bands λ 4695, λ 4760 and λ 4825 are all shifted to the red at the higher temperature, and especially λ 4825, the shift in this case amounting to 5 A. U. In the case of these bands the shift is not an apparent one due to unsymmetrical broadening, for in this instance there is no broadening at all.

The band from λ 5710 to λ 5860 at 6° has widened very unsymmetrically and has the limits λ 5710 to λ 5920. The short wave length side is quite sharp and its position is practically independent of the temperature. The long wavelength edge is quite broad and recedes quite rapidly towards the red as the temperature is raised. The bands in the red, $\lambda\lambda$ 6810 and 6900, grow fainter and fainter with rise in temperature, and have practically disappeared at 82°. The band λ 6245 is very weak at 6° and has disappeared at about 60°.

It will thus be seen that not only does the presence of calcium chloride modify greatly the absorption of neodymium chloride, but that it changes the effects due to temperature very fundamentally. In pure neodymium chloride practically no bands decrease in intensity with rise in temperature, and at present no shift has been detected. When calcium chloride is added to the solution most of the bands decrease in intensity with rise in temperature and several are shifted towards the red at the same time. Several bands disappear. Moreover, although the band $\lambda\lambda$ 6800 to 6900 widens, this widening is entirely on the red side, whereas for the pure neodymium chloride solution this widening always takes place on both sides of the band.

A spectrogram, B, Plate XXI, was made to show the effect of change in temperature upon a 2.15 normal aqueous solution of neodymium nitrate. The length of layer was 3 mm. The exposures were for 40 seconds to the Nernst glower (current 0.8 ampere, slit width 0.20 mm.). The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison spark, the temperatures were 4°, 17°, 29°, 43°, 58°, 71° and 84°.

The changes in the spectrum due to this change in temperature of 80° were very slight. The NO$_3$ band extends to about λ 3250 at 4°, and to about λ 3280 at 84°. The bands at λ 3500 became considerably wider and their edges more diffuse at the higher temperatures. At the lower temperatures fine bands appear at $\lambda\lambda$ 5210, 5225 and 5240. At 84° these bands all merge into a single band. The red band extends from λ 5705 to λ 5860 at 4°. The band at λ 5820 is very faint at the lower temperatures. At 84° it is unrecognizable. At this temperature the red band extends from λ 5700 to λ 5880. The widening of this band for the concentrated solution is somewhat greater than for the dilute solution, but the effect of concentration is very slight. This is to be expected since the effect of temperature itself is so very minute.

A spectrogram, A, Plate XXIII, was made of a 1.66 normal aqueous solution of neodymium bromide 54.6 mm. deep. The exposures were 3 minutes to the Nernst glower and 6 minutes to the spark. The current in the Nernst glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison scale, the temperatures were 6°, 20°, 33°, 47°, 62°, 73° and 82°.

The effect of rise in temperature on the absorption spectra of this salt was quite marked, practically all of the bands broadening and becoming more intense. At 6° the ultraviolet absorption extended to λ 3600. At 82° it had advanced to λ 3800. Very narrow and fine bands appear at $\lambda\lambda$ 4186, 4300, 4308, 4345, 6240, 6265, 6290, 6305, and much broader bands at λ 6380 and λ 6740. Wide bands occur from $\lambda\lambda$ 4390 to 4480, $\lambda\lambda$ 4550 to 4850, $\lambda\lambda$ 4990 to 5340, $\lambda\lambda$ 5650 to 5950 and $\lambda\lambda$ 6760 to 6930, at 6°. At 82° these bands have the following limits, respectively: $\lambda\lambda$ 4380 to 4500, $\lambda\lambda$ 4540 to 4910, $\lambda\lambda$ 4960 to 5370, $\lambda\lambda$ 5620 to 5990 and $\lambda\lambda$ 6730 to 6960.

Erbium Chloride. A spectrogram, B, Plate XXIII, was made to show the effect of rise in temperature on the absorption spectrum of a solution of erbium chloride. For this purpose a 0.94 normal solution was used and the depth of layer was 48 mm. The solution probably contained a con-

siderable number of impurities, so that the amount of erbium was in fact quite small. The absorption spectrum was found to change but little with rise in temperature, thus indicating a dilute solution. Exposures were made for 30 seconds to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the spectrum nearest the comparison scale, the temperatures were 7°, 17°, 29°, 46°, 60°, 70° and 80°.

At 70° the ultraviolet is absorbed to λ 3950. As the temperature is raised the ultraviolet absorption increases, and at 80° it reaches λ 3150. Bands from 20 to 40 A. U. wide occur at λ 3235, λ 3510, λ 3640 and λ 3785. These bands are slightly wider at 80°, but as for all the other erbium bands this widening is very small. Weak and narrow bands appear at $\lambda\lambda$ 4165, 4425, 4458, 4500 (strong), 4535, 4540, 4555, 4580, 4685, 4750 (30 A. U. wide), 4810, 4840, 4855, 4870 (strong and 20 A. U. wide), and 4920. λ 4920 lies alongside of a fuzzy band extending from λ 4910 to λ 4950.

After these comes a rather wide band which for a shorter length of layer would most likely be broken up into a number of much finer bands. This band extends from λ 5190 to λ 5250. At λ 5217 a narrow sharp line runs through the fuzzier and wider band. Broad (about 30 A. U. wide) and very faint bands are located at λ 5630 and λ 5760. For greater concentrations these would probably show as finer bands. The band at λ 6540 is much more diffuse on the red than on the violet side, this possibly being due to a component that is not separated at this temperature. Other bands are located at $\lambda\lambda$ 5365, 5380, 5425, 5445, 5505, 6410, 6440, 6495 and 6690.

The general effect of rise in temperature here is to cause the lines to become slightly fuzzier and to show more of a "washed out" appearance. No shift due to rise in temperature was noticed.

Throughout all the previous work the wave lengths were read directly from a scale. This scale was made so as to give the wave lengths in A. U. directly. It was found in the meas-

Plate XXIII.

B

A
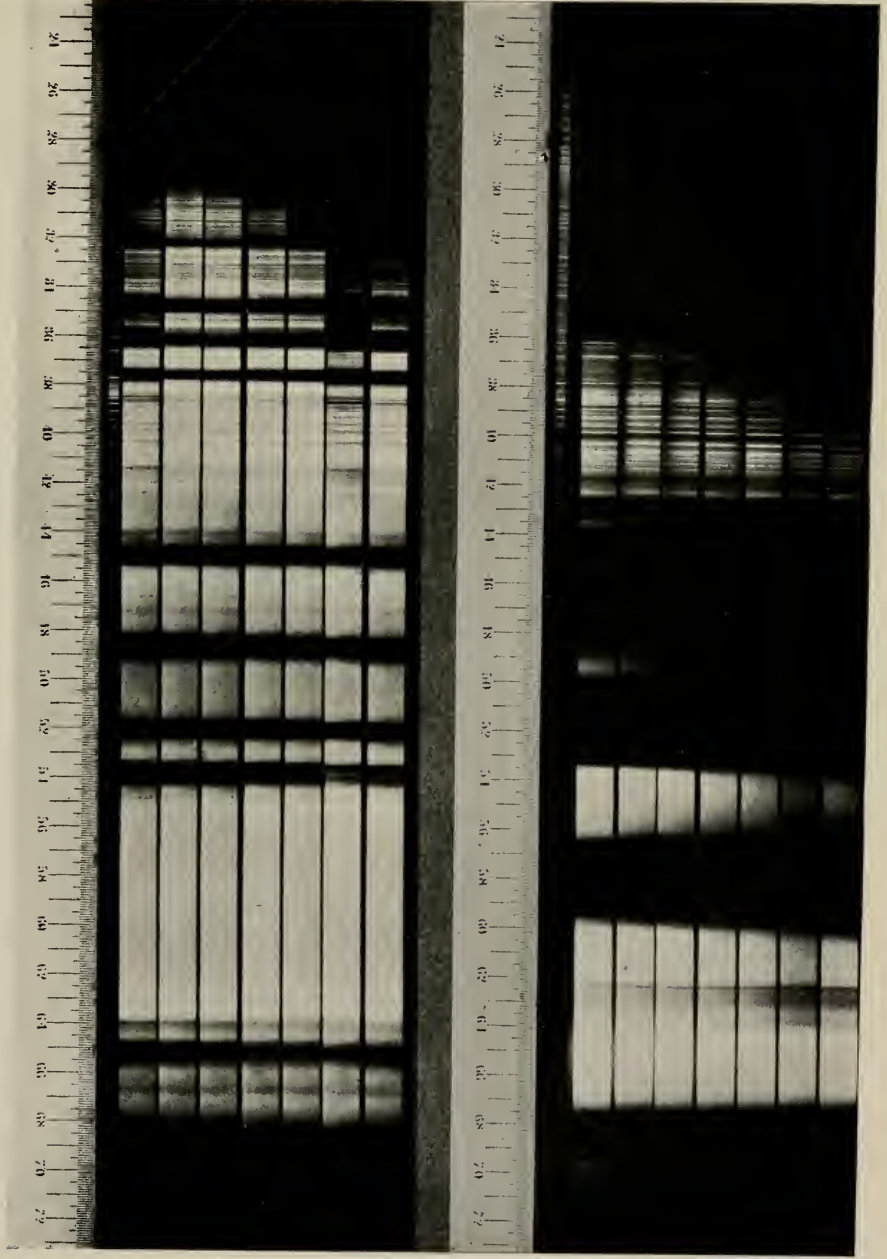
urements that the Seed films did not correspond to the Wratten and Wainwright films when the same spark spectra on the two kinds of films were placed beside one another. This was probably due to different shrinkage of the two kinds of films on fixing, washing and drying. For this reason the wave length measurements are not absolutely correct but only relatively so. All the temperature work was done with Wratten and Wainwright films. The relative measurements of fine bands for any spectrogram are probably correct to within a few Angström units.

IV. General Results.

In the present spectroscopic investigation our working hypothesis has been that the valency of any atom or radical is due to electrons, and in a compound there are electrons that are outside of the atoms. The charged systems within the atom are supposed to be neutralized so that their electric fields do not extend far from the system. To visualize an atom we must consider that if the whole mass were electromagnetic and the components were electrons, then these electrons would occupy relatively about as much of the space in an atom as the planets do in the solar system. Light waves then would be very large as compared with the atoms, and if the electron systems within the atom are neutralized and the elastic forces large, the absorption of energy would be very small, so that the body will be practically transparent.

It seems quite possible that the second kind of wide absorption bands may be due to the absorption by the valency electrons, or, in the case of the infra red bands, by the ions themselves. The valency electrons and ions will be very greatly modified by the solvent and any foreign salts, such as calcium or aluminium compounds, dissolved in it.

In discussing gas spectra we found that the prevalent belief is that gases radiate and absorb line spectra only when the atoms or molecules are in a peculiar condition. In some cases this condition may be brought about by intense ionization. It is quite probable that when a light wave passes over the UO_2 group or any other group the valency electrons

are set into vibration, and in some cases may even be torn off from the group. This would subject the outer electron systems of the uranium atom to intense electrical forces, and it seems quite possible in this case that the uranium or neodymium atom may be able to absorb or emit a rather fine band spectra. In the case of a gaseous atom or molecule the time between collisions is quite long compared with the frequencies of the light vibrations, and the vibrating electron systems are probably far inside the atom and therefore but slightly affected by neighboring molecules and various physical and chemical changes in the neighborhood. In the case of the vibrating systems of uranium, neodymium and erbium salts, the outside physical and chemical conditions play a very important rôle. Now in the case of a hydrated molecule or ion containing the UO_2 group, it seems that it would be possible to get some knowledge of the forces resulting from an atmosphere if the value of e/m for the various light vibrators were known. In the same way it may be possible to find the effect of the NO_3 group.

Rise in temperature causes the general absorption of any salt in water to increase and also causes the bands to broaden and become more intense.

In general, the increase of the general absorption with rise in temperature is much greater for concentrated solutions. This also holds true for bands of the second type, and to a small extent for bands of the third type.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge with rise in temperature.

The uranyl chloride bands are shifted towards the red with rise in temperature. No shift for the uranyl nitrate could be noticed. The uranyl acetate and sulphate bands were slightly shifted.

No shift with rise in temperature was noticed for solutions of neodymium or erbium salts. When calcium chloride is present the neodymium chloride bands are, however, shifted, and the remarkable fact is observed that the bands then become fainter with rise in temperature. This latter phenom-

enon is considered to be very important, and it may be that the abnormal Zeeman effect observed by Becquerel is due to the presence of foreign compounds in the tysonite and xenotine crystals.

In concluding, the authors wish to express their thanks to Drs. Pfund and Anderson for many valuable suggestions. They also wish to thank Prof. Ames for the grating and for the ideal conditions under which the work is being done.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY, October, 1909.

TETRABROMDIKETOCYCLOPENTENE.

By C. LORING JACKSON AND H. A. FLINT.

In 1906 F. W. Russe and one of us published[1] a description of a substance prepared by the action of fuming nitric acid and bromine on tetrabrom-*o*-quinone, which had the formula $C_5Br_4O_2$, and was supposed to be a cyclopentene-*o*-quinone. The present paper contains a study of this compound, to which we had hoped to add an account of a white acid containing bromine formed at the same time, but we have not succeeded in finding the conditions under which this acid is formed, obtaining oxalic acid invariably in place of it.

In studying the constitution of the yellow compound melting at 142°, we found that a solution of sodic carbonate decomposed it, giving as the principal product a black tar soluble in water, and in smaller amounts dibrommaleic acid (identified by its melting point, 123°, its properties, and an analysis), and some bromine derivative of methane, which we suppose to be methylene bromide, but the quantity was too small to settle this point with certainty. On these observations we founded a lactone formula, which explained all the observed facts; but, when our work had reached this stage, there appeared a paper by Franz Henle[2] describing a yellow

[1] THIS JOURNAL, **35,** 184 (1906).
[2] Ann. Chem. (Liebig), **352,** 45 (1907).

compound made from the tribromtriketocyclopentane of Hantzsch[1] by the action of phosphoric pentabromide, which, like ours, had the formula $C_5Br_4O_2$, melted at 142°, and agreed with ours in its other properties. To make certain that this compound was identical with ours, some of it was made by Henle's method, and treated with methyl alcohol, when it gave a product, $C_5Br_3OCH_3O_2$, melting at 67°, and with ethyl alcohol a compound, $C_5Br_3OC_2H_5O_2$, melting at 110°; as our compound also gives these derivatives there is no question that these substances are the same.

This identification of our compound with Henle's made it necessary to substitute for our lactone formula that of a cyclopentene, which had been proved to be the correct one, as follows: Hantzsch found that his tribromtriketocyclo-pentane (made by the action of bromine on a solution of sodic bromanilate) was decomposed by boiling with bromine water into hexabromacetone and oxalic acid. Its constitution therefore must be represented by Formulas I and II,

$$
\begin{array}{ccc}
\overset{HBr}{O=C-C} & \overset{Br}{HO-C=C} & \overset{Br}{BrC=C} \\
\underset{O=C-C}{}\!\!>C=O & \underset{O=C-C}{}\!\!>C=O & \underset{O=C-C}{}\!\!>C=O, \\
\underset{Br_2}{} & \underset{Br_2}{} & \underset{Br_2}{} \\
\text{I.} & \text{II.} & \text{III.}
\end{array}
$$
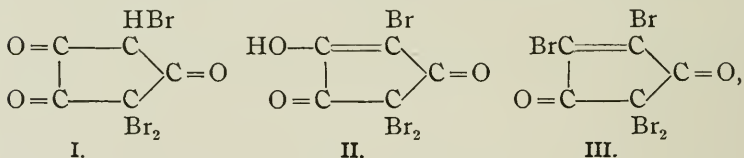
I representing the keto, II the enol form. Henle's treatment of this with phosphoric pentabromide replaced the hydroxyl in II by bromine, giving III as the formula for our compound, which is therefore the tetrabromdiketocyclopentene. This formula is in harmony with its conversion into dibrommaleic acid and methylene bromide observed by us, and with all our other observations.

The conversion of tetrabrom-*o*-quinone into the tetrabrom-diketocyclopentene offers no difficulties, but as none of the intermediate products have been isolated we do not think it worth while to consider the different series of reactions which may have taken place in this transformation.

Tetrabromdiketocyclopentene is a substance with sharply

[1] Ber. d. chem. Ges., **21**, 2421 (1888).

contrasted properties. On the one hand, it is remarkably stable in presence of acids: for instance, it can be boiled for several hours with fuming nitric acid without visible effect, and bromine, either alone or with water, has no action on it. On the other hand, water, when boiled with it, or ethyl or methyl alcohol, an alkali, or even sodic acetate in the cold decomposes it with great ease. A remarkable instance of this difference in behavior is found in the fact that it can be boiled without action with bromine and water, whereas similar boiling with water alone would produce a small amount of a soluble black decomposition product. It is then, apart from the action of acids, a very reactive substance, and we have prepared from it the following compounds:

With aniline it gives two compounds, one,

$$C_5Br_3(C_6H_5NH)O_2,$$
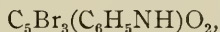
yellow needles melting at 178°; and a red amorphous body, which does not melt below 300°, and has the composition

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2.$$

Sulphurous dioxide with alcohol and water replaces two atoms of bromine by hydrogen, forming the compound $C_5H_2Br_2O_2$, yellow plates melting at 151°. Phenylhydrazine gives with this dibromdiketocyclopentene a brown amorphous product not melting below 300°, which, on analysis, gave results agreeing with the calculated values for

$$C_5H_2(C_6H_5N_2H_2)_2O(C_6H_5N_2H).$$
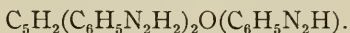
Aniline gives with the compound $C_5H_2Br_2O_2$ yellow needles melting at 121°, and having the formula

$$C_5H_2Br(C_6H_5NH)O_2,$$

which are also made by the reduction of tribromanilinodiketocyclopentene (melting point 178°) with sulphurous dioxide. Sodic carbonate in aqueous solution in the cold converts the body $C_5H_2Br(C_6H_5NH)O_2$ into a substance having the composition $C_6H_5NHC_3HO$, yellow needles melting at 221°. Methyl alcohol acts on tetrabromdiketocyclopentene even in the cold, giving the compound $C_5Br_3(OCH_3)O_2$, white needles melt-

ing at $67°$. Ethyl alcohol, under the same conditions, gives the ethyl derivative, $C_5Br_3(OC_2H_5)O_2$, white needles melting at $110°$. It is noteworthy that in this case the ethyl compound has the higher melting point of the two. Aniline acts on the tribromethoxydiketocyclopentene, giving the compound

$$C_5H_2(OH)(C_6H_5NH)O_2,$$
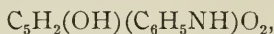
red and amorphous, melting with decomposition at $140°$. The presence of the hydroxyl was confirmed by the formation of the acet compound,

$$C_5H_2(OC_2H_3O)(C_6H_5NH)O_2,$$
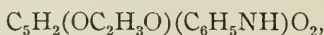
amorphous, pale brown, melting at $150°$ with decomposition.

In determining the positions of the different radicals in the cyclopentene ring we start from the compound

$$C_6H_5NHC_3HO,$$

melting at $221°$, made by the action of sodic carbonate on the bromanilinodiketocyclopentene,

$$C_5H_2Br(C_6H_5NH)O_2,$$

melting at $121°$. If this compound has the simplest possible molecular weight, containing but one benzene ring, we can find only three possible formulas for it:

I. $(C_6H_5NH)CH = C = CO$;

II. $(C_6H_5NH)—CO—C \equiv CH$;

$$\text{III. } (C_6H_5NH)—C\overset{\displaystyle CH}{\underset{}{\diagup\diagdown}}CO.$$
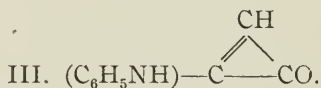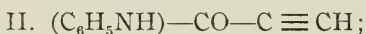
I, a ketene, and II, an acetylene, must be exceedingly reactive substances. They must therefore add bromine easily and be promptly attacked by potassic permanganate. Our substance reacts with bromine only after standing over half an hour, and with permanganate the reaction was not complete even after 24 hours; in other respects also it is decidedly sluggish. Formulas I and II, therefore, must be rejected, and III adopted for our substance, which makes it an anilinoketotriene. All its observed properties are such as would

be expected from this formula; thus, it was decidedly stable and was attacked slowly by bromine or potassic permanganate; oxidations gave products without pronounced acid properties; phenylhydrazine reacted with it, and it did not precipitate silver from ammoniacal argentic nitrate. This view of its structure, however, cannot be considered finally established, as it is possible that it may have a larger molecular weight, having been formed by the union of two residues of the cyclopentene to form a ring of more than 3 atoms of carbon—a view which is certainly supported by its high melting point, 221°. Unfortunately, we did not determine its molecular weight, which would have settled the question, so that we can adopt this triene formula only provisionally as one which gives an excellent explanation of the observed facts.

For determining the positions of the radicals in the pentene ring it makes no matter whether the substance is a triene or has a more complex formula, as our argument applies equally well in either case. There are four possible formulas for the bromanilinodiketocyclopentene, from which the triene was formed:
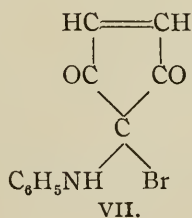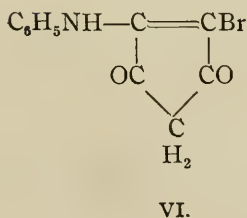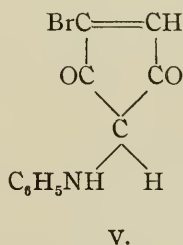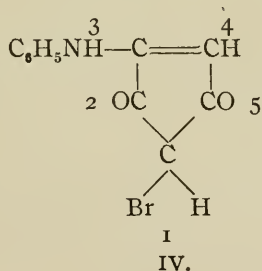
The formation of dibrommaleic acid and methylene bromide, when the compound $C_5Br_4O_2$ is treated with sodic carbonate, makes it probable that if formula V or VII were correct the anilino group would split off attached to one atom of carbon instead of to three, as in our experiment, since in these formulas it is attached to the atom of carbon which was eliminated as methylene bromide from the tetrabrom compound. If, however, either of these substances (V or VII) could form an anilinotriene, it could not have the formula C_6H_5NHCHO found by us, but would contain at least 2 atoms of oxygen. Formulas V and VII must therefore be rejected. The same reasoning applies to VI, which might form a triene, but this would contain two atoms of oxygen, as the atom of bromine would certainly have been replaced by a hydroxyl. Formula VI, therefore, must also be rejected, which leaves Formula IV as the only one possible. That is, the anilino group enters the pentene ring at 3, if we adopt the numbering of the places given with Formula IV.

As the anilino compound, $C_5H_2Br(C_6H_5NH)O_2$, is formed from the dibromdiketocyclopentene, $C_5H_2Br_2O_2$, by replacing one atom of bromine by the anilino group, it follows that this also has the same constitution, $[1,4]H_2[1,3]Br_2$. It certainly would not have been expected that the two atoms of bromine replaced in the reduction would be attached to different parts of the pentene ring, but this is not without analogy, as Hantzsch[1] has observed with chlorpentacarbon rings that only one of the atoms of chlorine in the group CCl_2 is replaced by hydrogen. This view of the structure of the dibrom body is supported by the observations that it gives no methylene bromide when treated with sodic carbonate, and that it is not attacked by alcohol.

The anilino derivative, $C_5Br_3(C_6H_5NH)O_2$, made from the tetrabrom compound, $C_5Br_4O_2$, and melting at 178°, was converted into the monobrom compound,

$$C_5H_2Br(C_6H_5NH)O_2,$$

melting at 121°, on reduction with sulphurous dioxide. The

[1] Ber. d. chem. Ges., **22**, 1238, 2841 (1889).

anilino group must therefore be at 3 in this body; and, as this bromanilino compound, melting at 178°, can be converted by alcohol and aniline into the anilinohydroxydiketocyclopentene, $C_5H_2(OH)(C_6H_5NH)O_2$, melting at 140°, it follows that the anilino radical is at 3 in this compound also. Another way of making this hydroxy derivative was by the action of aniline on the tribromethoxydiketocyclopentene,

$$C_5Br_3(OC_2H_5)O_2,$$

melting at 110°; it follows therefore that the ethoxyl does not enter the ring at the same place as the anilino group. Its position can be made out from the fact that sodic methylate gave dibrommaleic acid with tetrabromdiketocyclopentene, and as it does not seem possible that methyl (or ethyl) alcohol should attack the ring at a different place from sodic methylate, it follows that neither the bromine at 3 nor at 4 could have been replaced, as that would have given brommethoxymaleic acid instead of dibrommaleic acid. This leaves only the constitution $C_5[1,3,4]Br_3[1](OCH_3)$ (or $OC_2H_5)O_2$ for these compounds, and the anilino derivative melting at 140° must be $C_5[1,4]H_2[1]OH[3](C_6H_5NH)O_2$. In the formation of this last substance from the compound $C_5Br_3(OC_2H_5)O_2$ two atoms of bromine have been replaced by hydrogen—a reaction, which it is easy to understand, when aniline is present; and the ethoxyl has been saponified to hydroxyl, which it is harder to explain, but it may have been due to the action of the water in the ether used as a solvent.

The phenylhydrazine derivative of dibromdiketocyclopentene, $C_5H_2Br_2O_2$, would have the structure

$$C_5[1,4]H_2[1,3](C_6H_5N_2H_2)_2[2](C_6H_5N_2H)[5]O.$$
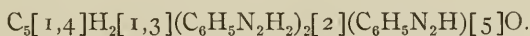
The action of the phenylhydrazine on one of the keto groups only is in harmony with the observations of Hantzsch and Zincke with other diketopentacarbon rings. The composition of this substance furnishes a partial confirmation of the constitution $C_5[1,4]H_2Br_2O_2$, assigned to dibromdiketocyclopentane, for, if the two atoms of bromine had stood at 1,1, only two phenylhydrazine residues would have entered the

molecule; the presence of 3 therefore excludes one of the 3 possible formulas; but in considering this argument and the structure worked out for this compound it must be remembered that it is amorphous and melts above 300°, which may indicate a more complex formula than the one adopted by us. The same doubt applies to the only substance still unconsidered, the compound $C_5OH(C_6H_5NH)(C_6H_5N)O_2$, as it is also amorphous, and does not melt below 300°. Although the formula given agrees best with the analyses, it is not established with certainty, since the formula

$$C_5H(OH)(C_6H_5NH)_2O_2$$
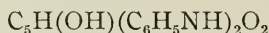
gives percentages not very far removed from those obtained experimentally, and one cannot have much confidence in a purification effected by washing only. Under these conditions we think it not worth while to discuss the constitution of this body.

<div align="center">EXPERIMENTAL PART.</div>

Preparation of Tetrabromdiketocyclopentene, $C_5Br_4O_2$.—Twenty grams of tetrabrompyrocatechin (or tetrabrom-*o*-quinone) were mixed with 100 cc. of fuming nitric acid and 10 cc. of bromine, and the mixture heated on the steam bath in a flask until all the bromine had been given off, which usually took 30–40 minutes. The hot solution was then diluted with about 250 cc. of water, which threw down the product, either as a finely divided precipitate or as a reddish brown oil; in either case it was heated with the dilute nitric acid on the steam bath with constant stirring until it was converted into large yellow crystals. These were filtered out, washed thoroughly with water, and recrystallized from a mixture of equal parts of benzene and ligroin, until they showed the constant melting point 142°.

The method described above is essentially that by which the substance was first prepared by Russe and one of us.[1] In that work, however, the yellow product was accompanied by a white acid containing bromine. We at first tried to prepare this white acid by evaporating the aqueous mother

[1] This Journal, **35**, 184 (1905).

liquors, from which the yellow crystals had been deposited, but the product was nothing but oxalic acid containing a trace of these crystals. As the acid containing bromine might have been oxidized to oxalic acid by the evaporation with nitric acid, an attempt was next made to obtain it by shaking out the mother liquors with ether, but here also the extract, of which there was very little, proved to be nothing but oxalic acid. That the substance was oxalic acid was shown by its calcium, ammonium and aniline salts. The last melted at 170°–180°, and by melting was converted into oxanilide melting at 242°. In spite of many experiments we have not succeeded in reproducing the conditions under which Russe's white acid was formed. That this was not oxalic acid was proved by its melting point, 144°–146°, and by a number of analyses made by Dr. Russe, which gave large percentages of bromine, but, as the substance used evidently was not fully purified, it is not worth while to publish them.

Composition of the Tetrabromdiketocyclopentene.—In order to collect in this paper all the data in reference to this subject, we repeat the analyses and properties[1] already published by Russe and one of us:

	Calculated for $C_5Br_4O_2$.	I.	II.	III.	IV.
			Found.		
C	14.57	15.17	14.43	. . . .	. . . .
H	0.00	0.35	0.19	. . . .	. . . .
Br	77.67	. . . .	. . . .	77.67	77.69

"*Properties.*—It crystallizes from fuming nitric acid in thick plates, from a mixture of benzene and ligroin in large prisms, which are apparently monoclinic. Its color is a full yellow like that of potassic chromate. It melts at 142° with no signs of decomposition, and is soluble in alcohol, ether, chloroform, benzene, or acetone; slightly soluble in ligroin; insoluble in water."

Various Reactions of Tetrabromdiketocyclopentene.—This substance was very little affected by cold water even when shaken with it for a week, but, if boiled with water, it was decomposed, forming in a few hours a very dark solution which

[1] THIS JOURNAL, **35**, 185 (1905).

gave a test for hydrobromic acid. An aqueous solution of sodic acetate acted on it even in the cold, forming a dark-colored solution, which, after acidification, gave on extraction with ether a viscous product. With an aqueous solution of sodic carbonate a similar result was obtained, which will be described in detail later in this paper. The hydrochloride of hydroxylamine reacted with it, when the mixture was warmed on the steam bath, but no definite product could be isolated. The substance also reacted with methyl or ethyl alcohol in the cold, forming compounds which will be described in a later paragraph.

The action of zinc and dilute sulphuric acid or of a warm aqueous solution of stannous bromide seemed to produce a far-reaching decomposition, which may have been due to the action of the water, while sulphurous dioxide with alcohol and water brought about the replacement of two atoms of bromine by two of hydrogen. The action of aluminum amalgam and alcohol for an hour on the steam bath gave no reduction, the product being the ethoxy compound; and sodium in dry ether had no action whatever.

On the other hand, this substance, which is so sensitive toward water, alcohols or alkalies, shows a marked stability toward some other classes of reagents. Bromine, for instance, has no action on it, as was shown by dissolving some of the substance in glacial acetic acid, adding two drops of bromine, and allowing the solution to stand overnight at ordinary temperatures. In the morning the color of the solution was essentially unchanged, and the original compound was recovered from it unaltered. A similar result was obtained when chloroform, carbonic tetrachloride or carbonic disulphide was used as the solvent instead of glacial acetic acid. In fact the presence of bromine prevented the action of water on it, for one gram of the substance, after being warmed with bromine and water for four hours, was recovered unchanged, whereas water alone would have caused a considerable decomposition under these conditions. This resistance to acid oxidizing agents was also shown by boiling it for four hours with fuming nitric acid with no effect. A neutral solution of

potassic permanganate decomposed it, to be sure, but this, was undoubtedly on account of the water and the alkali formed in the reaction. It was also unaffected by acids, such as strong sulphuric acid, whether hot or cold, or diluted with water, or with water and alcohol, or dilute nitric acid, or a solution of hydrobromic acid, even when heated with it for several hours on the steam bath. Glacial acetic acid too produced no effect on it, and the same was true of acetic anhydride, acetyl chloride, or benzoyl chloride. We have then a substance showing a really extraordinary resistance toward acids or oxidizing agents, but attacked with such ease by water, alcohols or alkaline solutions that this property forms a serious obstacle in the way of studying the action of various reagents upon it.

Action of Sodic Carbonate in Aqueous Solution on Tetrabromdiketocyclopentene.—Ten grams of the substance were mixed with 20 grams of sodic carbonate dissolved in 150 cc. of water and the mixture allowed to stand in a corked Erlenmeyer flask at ordinary temperatures for several days, with occasional shaking. The aqueous liquid soon turned dark, and, as the solid disappeared, the color deepened, until it was black and nearly opaque. The product was worked up after the substance had dissolved, which happened in less than a week. As the liquid smelt of some bromine derivative of methane, it was extracted with ether, which, on careful evaporation, left a small amount of a dark liquid with an odor like that of bromoform, but it appeared in such small quantities that in order to obtain enough to purify for analysis and a determination of the boiling point, it would have been necessary to devote to the experiment an outlay of time and labor out of all proportion to the value of the result. All our experiments on this body, including the formation of phenyl isocyanide, seemed to indicate that it was bromoform, but, as no explanation can be found for the formation of bromoform under these conditions from the tetrabromdiketocyclopentene, we are inclined to think, in the absence of convincing experiments, that it was methylene bromide, which would be the natural product of the decomposition.

The alkaline aqueous liquid, after the extraction with ether, was acidified with sulphuric acid, and, as no precipitate was formed, again extracted with ether several times, which removed from it a black, sticky, tarry mass easily soluble in ether, water, or alcohol, but nearly insoluble in the other common solvents. The preparation of a definite compound from this product gave much trouble, but after several experiments we finally succeeded by using the following method: The tarry mass, after it had stood for several weeks until it had partially solidified, was treated repeatedly with toluene, to which a few drops of alcohol had been added. The solutions thus formed, when poured off and evaporated to dryness, gave solid residues, which in different experiments varied from brown to nearly white; they were purified by many recrystallizations from toluene with a few drops of alcohol, until they became pure white and showed the constant melting point 123°, when the substance was dried *in vacuo* for analysis.

The yield at best would have been small, as in the process two of the four atoms of bromine were removed, but it was still more diminished by the formation of the black tar, which was the principal product of the action, the amount of the white substance being so minute that many preparations were necessary to obtain enough of it for analysis. As, too, its purification was very laborious, this work occupied not far from a year.

I. 0.1157 gram of the white acid gave 0.1583 gram AgBr.

II. 0.1654 gram substance gave 0.2266 gram AgBr.

	Calculated for $C_4Br_2O_4H_2$.	Found. I.	II.
Br	58.38	58.24	58.30

These analyses agree therefore with the calculated values for dibrommaleic acid, and that the substance is this acid is proved by the melting point, 123° (Ciamician and Silber[1] give 123°.3), and the other properties, which were as follows: White needles easily soluble in water, alcohol, methyl alcohol, ether, or acetone; nearly insoluble in the other common

[1] Ber. d. chem. Ges., **17**, 558 (1884).

solvents. Strong hydrochloric acid has no visible effect on it; strong nitric acid, when warm, converts it into oxalic acid, hydrobromic acid, and carbonic dioxide; strong sulphuric acid dissolves it. The calcium and barium salts are white and soluble, the lead and silver salts white precipitates; the latter explodes on heating.

The black liquid formed by the action of sodic carbonate on tetrabromdiketocyclopentene contained a larger amount of sodic bromide than would correspond to the formation of dibrommaleic acid. This was not unexpected, however, as much of this acid might have suffered a further decomposition, and also a larger amount of the bromide might have been formed in the reaction leading to the black tar, which was the principal product of this reaction. This tar was soluble in water, ethyl or methyl alcohol, or ether, and apparently a large part of it was left in the aqueous liquid, after it had been extracted thoroughly with ether. Although we have devoted a great deal of time and work to this substance, we have not succeeded in extracting from it any definite compound except the dibrommaleic acid.

Action of Sodic Methylate on Tetrabromdiketocyclopentene.— Five grams of the substance mixed with a methyl alcohol solution of an excess of sodic methylate were allowed to stand several days at ordinary temperatures, until all the solid had disappeared. The very dark solution was then saturated with carbonic dioxide and the precipitated salts filtered out. As the filtrate gave no appreciable amount of organic residue after evaporation, the product of the reaction was sought in the precipitate by dissolving it in dilute nitric acid and extracting several times with ether, which, on evaporation, left a dark tarry mass. By treating this with toluene and a few drops of alcohol, and purifying by recrystallization from the same mixture of solvents, dibrommaleic acid was isolated and recognized by its melting point, 123°, its solubility in the organic solvents, and the solubilities of its calcium, barium, lead and silver salts. Sodic methylate, in a solution of methyl alcohol, therefore acts on tetrabromdiketocyclopentene in the same way as an aqueous solution of sodic carbon-

ate. Sodic ethylate gave a black, sticky mass, similar to that obtained with the methylate. It was not thought worth while to study it further.

Action of Aniline on Tetrabromdiketocyclopentene.

I. Tribromanilinodiketocyclopentene, $C_5Br_3(C_6H_5NH)O_2$.—Ten grams of tetrabromdiketocyclopentene and 10 cc. of aniline were dissolved in 300 cc. of ether, when a precipitate of hydrobromide of aniline was thrown down immediately. The mixture was allowed to stand a few minutes with occasional shaking, until no further precipitate was formed, after which it was filtered and the filtrate evaporated to about one-half its volume, when, upon adding a large excess of ligroin, a brown precipitate was obtained, and this was filtered out and recrystallized from a mixture of equal parts of benzene and ligroin, until it showed the constant melting point 178°, when it was dried *in vacuo* for analysis.

I. 0.2027 gram substance gave 0.2684 gram AgBr.
II. 0.2214 gram substance gave 0.2941 gram AgBr.

	Calculated for $C_5Br_3C_6H_5NHO_2$.	Found.	
		I.	II.
Br	56.60	56.35	56.53

Properties of Tribromanilinodiketocyclopentene.—Yellow needles, which melt at 178° without decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, or acetone; moderately soluble in benzene, toluene, or glacial acetic acid; insoluble in cold ligroin, more soluble when it is hot. Strong hydrochloric acid has no effect on it, whether hot or cold; strong nitric acid gives a yellow solution, from which water precipitates nothing; strong sulphuric acid gives an orange solution, from which water apparently precipitates the original substance. Aqueous sodic hydrate gives a yellow solution with it, having the characteristic odor of phenyl isocyanide. A solution of sodic carbonate formed a brown solution, from which, after acidification, a dark oil can be extracted with ether. An excess of aniline, warmed with an alcoholic solution of the substance, forms a red amorphous product, described in the next section.

The behavior of tribromanilinodiketocyclopentene with the following reagents was also studied. Water warmed with it on the steam bath for three hours attacked it slightly, forming a brown solution, which, on evaporation, yielded only a little tar and hydrobromide of aniline. Alcohol had no effect on it after standing at ordinary temperatures for 2 days, or boiling for 3 hours. Acetic anhydride had no action on it even after standing overnight. Phenylhydrazine was mixed with a solution of it in chloroform and alcohol; the mixture was warmed on the steam bath and then allowed to stand at ordinary temperatures for a day; the product was a brown mass decomposing at 135°–140°, from which we did not succeed in isolating any substance fit for analysis. Two grams of the aniline compound were dissolved in glacial acetic acid, a few drops of bromine added, and the mixture allowed to stand for 3 days. On diluting with water two different substances were obtained, one of which was yellow and melted at about 138°, the other nearly white and melted at about 145°, but as we thought it probable that part of the bromine had entered the phenyl group, we did not think it worth while to take the time to study them.

II. Hydroxyanilinoanildiketocyclopentene,
$C_5OH(C_6H_5NH)(C_6H_5N)O_2$.—This substance was formed instead of the monoanilino compound just described, when tetrabromdiketocyclopentene was heated with aniline and alcohol as follows: Five grams dissolved in 95 per cent. alcohol and mixed with 10 cc. of aniline were warmed for half an hour on the steam bath, when, on cooling, the dark reddish-brown liquid deposited a dark red product, which was filtered out. All attempts to purify this substance by recrystallization failed, since the only liquid which dissolved it freely enough was aniline, and from this no good crystals could be obtained; it was therefore washed with alcohol, water, alcohol again, and ether, after which it was dried *in vacuo* for analysis:

I. 0.1782 gram substance gave 0.4643 gram CO_2 and 0.0730 gram H_2O.

II. 0.1687 gram substance gave 0.4351 gram CO_2 and 0.0584 gram H_2O.

III. 0.1988 gram substance gave 17.9 cc. N_2 at 29° and 753 mm.

IV. 0.2394 gram substance gave 21.3 cc. N_2 at 22°.7 and 757.1 mm.

	Calculated for $C_5OHC_6H_5NHC_6H_5NO_2$.	I.	II.	III	IV.
			Found.		
C	69.89	71.06	70.34	....	....
H	4.11	4.55	3.85	....	....
N	9.59	....	....	9.73	10.01

These analyses agree as nearly as could be expected from a substance which could be purified only by washing. The formula calculated from them would indicate that one of the atoms of bromine in the tetrabromdiketocyclopentene had been replaced by hydroxyl. There is a strong analogy for such a replacement in the action of aniline on the ethoxy compound, $C_5Br_3OC_2H_5O_2$, which, as described later in this paper, forms a body having the composition

$$C_5H_2OH(C_6H_5NH)O_2,$$

and, as this is also formed by the action of aniline and alcohol on tribromanilinodiketocyclopentene,

$$C_5Br_3(C_6H_5NH)O_2,$$

it is evident that the hydroxy group can be introduced easily under these conditions. As the tribromanilino compound,

$$C_5Br_3(C_6H_5NH)O_2,$$
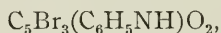
must be the first product of the action of aniline and alcohol on tetrabromdiketocyclopentene, it follows that they can convert this body either into the compound

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2$$

or

$$C_5H_2OH(C_6H_5NH)O_2,$$

according to the conditions under which they act.

Properties. It is a dark red amorphous powder which does not melt below 300° and is slightly soluble in hot alcohol, methyl alcohol, chloroform, benzene, toluene, or glacial acetic acid; insoluble in hot ether, or ligroin; very soluble in aniline,

but no good crystals could be obtained from this solution. Strong hydrochloric acid has no visible effect on it; strong nitric acid, or strong sulphuric acid, dissolves it. Sodic hydrate has no action on it at first, but after warming on the steam bath for several days it was found that part of the red solid had disappeared and there was a slight odor of phenyl isocyanide. Upon acidifying the solution with hydrochloric acid and extracting with ether only a little tar was obtained, and this looked so unpromising that it was not studied.

A substance with properties similar to those of the compound $C_5OH(C_6H_5NH)(C_6H_5N)O_2$ was formed by the longer action of aniline on the monoanilino body, $C_5Br_3(C_6H_5NH)O_2$, as a specimen of this compound, which had stood 4 days with aniline and ether, gave, after the aniline had been removed with hydrochloric acid and water, a brown residue, from which none of the monoanilino body could be extracted. It did not melt below 300°, was essentially insoluble in all the organic solvents, and contained no bromine, but to judge from its method of formation probably did not contain hydroxyl.

Reduction of Tetrabromdiketocyclopentene.

Dibromdiketocyclopentene, $C_5H_2Br_2O_2$,—The best method of obtaining this substance consisted in saturating with sulphurous anhydride a solution of several grams of tetrabromdiketocyclopentene in a mixture of three parts of water to one of alcohol and shaking the mixture for 10 to 12 hours. The solution was then filtered and the filtrate allowed to evaporate spontaneously, after which the slightly colored feathery crystals obtained were purified by crystallization from a mixture of equal parts of benzene and ligroin until they showed the constant melting point 151°, when they were dried *in vacuo* for analysis.

If a shaking machine is not available, the mixture can be allowed to stand overnight, but the product is less pure and abundant in this case. The liquid, after the reaction had taken place, gave a strong test for hydrobromic acid. The success of the process depended on using the proper proportions of water and alcohol. If more than one part of alcohol

to three of water was used the liquid took on a red color and the resulting crystals were also red, and in this case it was almost impossible to purify them. Even with 25 per cent. alcohol some of this red impurity was formed, but this was removed by the crystallization. We are unable to give any explanation of this color. If, on the other hand, the amount of alcohol was diminished, the reaction ran very slowly, so that standing for several days was necessary to get the result with a solution containing only 5 per cent. of alcohol, but, on the other hand, the product was free from color. Using the solutions hot, substituting methyl for ethyl alcohol, or passing the sulphurous dioxide into a moist benzene solution gave no better results.

I. 0.3255 gram substance gave 0.2762 gram CO_2 and 0.0280 gram H_2O.

II. 0.1268 gram substance gave, by the method of Carius, 0.1886 gram AgBr.

III. 0.1358 gram substance gave 0.1996 gram AgBr.

IV. 0.1453 gram substance gave 0.2149 gram AgBr.

	Calculated for $C_5H_2Br_2O_2$.	I.	II.	III.	IV.
			Found.		
C	23.62	23.14	....	....	....
H	0.79	0.96	....	....	....
Br	62.99	....	63.30	62.55	62.94

Properties of Dibromdiketocyclopentene.—It crystallizes in slightly yellow plates, which seem to belong to the orthorhombic system. It melts at 151° without decomposition and is easily soluble in ethyl or methyl alcohol or ether, but when such a solution is warmed for several hours, or allowed to stand in the cold for some days, decomposition sets in, as shown by the appearance of a dark color; soluble without decomposition, even when heated, in chloroform, benzene, toluene, or glacial acetic acid; slightly soluble in hot ligroin, but essentially insoluble in cold. The best solvent for it is a mixture of equal parts of benzene and ligroin. Strong hydrochloric acid has no effect on it; strong nitric acid, or sulphuric acid, dissolves it, when hot, apparently without decomposition, but dilute nitric acid on the steam bath gives oxalic

and hydrobromic acids; alkalies, including ammonic hydroxide, decompose it, forming a dark brown solution. Two grams of it were allowed to stand with sodic carbonate in aqueous solution for several days with occasional shaking, when a black solution was formed like that obtained from tetrabrom-diketocyclopentene, but no odor of any bromine derivative of methane was observed. The black solution was not studied.

Two grams of the dibromdiketocyclopentene were dissolved in glacial acetic acid or chloroform and a few drops of bromine added. The color of the bromine soon disappeared, and more was added in small portions as the color vanished, until an excess was present. Upon adding a quantity of water a precipitate was thrown down, which was proved by its melting point, 142°, and appearance to be the tetrabromdiketocyclopentene, $C_5Br_4O_2$.

Acetic anhydride left dibromdiketocyclopentene unaltered after standing overnight with it; but argentic acetate in alcohol in the cold gave a dark solution with a brown precipitate so finely divided that it could not be filtered out, but no argentic bromide. With dilute nitric acid in the cold the dibrompentene was converted in carbonic dioxide, oxalic acid and hydrobromic acid, or bromine. Potassic permanganate with sulphuric acid behaved in a similar way.

Action of Phenylhydrazine on Dibromdiketocyclopentene.— Ten cc. of phenylhydrazine were added to 2 grams of the substance dissolved in benzene, and the mixture, after warming on the steam bath, was allowed to stand overnight at ordinary temperatures. The brown amorphous body, which had separated, was washed with benzene, alcohol, a mixture of water and alcohol and ether, after which it was dried *in vacuo* for analysis:

I. 0.2064 gram substance gave 0.5224 gram CO_2 and 0.0803 gram H_2O.

II. 0.0867 gram substance gave 0.2210 gram CO_2 and 0.0458 gram H_2O.

III. 0.1428 gram substance gave 27 cc. N_2 at 23°.5 and 755.5 mm.

IV. 0.1467 gram substance gave 26.2 cc. N_2 at $16°.4$ and 764 mm.

Calculated for $C_5H_2(C_6H_5NHNH)_2(C_6H_5NHN)O$.	I.	Found. II.	III.	IV.
C	69.35	68.90	69.52	....	....
H	5.53	4.35	5.91	....	....
N	21.10	....	....	21.12	20.90

The analyses agree as well as could be expected from a substance which could be purified only by washing, and indicate that the substance was formed by replacing both the bromine atoms and one of the atoms of oxygen by phenylhydrazine groups, but the substance is so indefinite that its composition cannot be considered finally established. It is a brown amorphous powder which does not melt below 300°, is essentially insoluble in all the common solvents, but decomposed by both acids and alkalies.

Action of Aniline on Dibromdiketocyclopentene.

Bromanilinodiketocyclopentene, $C_5H_2Br(C_6H_5NH)O_2$.—When 7 grams of the reduced body were dissolved in ether, and 10 cc. of aniline added, hydrobromide of aniline appeared almost at once, but after standing at ordinary temperatures for several minutes with occasional shaking the precipitate ceased to form, and then it was filtered out and hydrobromic acid gas passed into the liquid until all the aniline was removed. The salt was filtered out and the filtrate, on evaporation to dryness, left a dark residue, which was extracted several times with a mixture of equal parts of benzene and ligroin. The yellow crystalline extract was purified by recrystallization from the same mixture until it showed the constant melting point 121°, when it was dried *in vacuo* for analysis—I.

The substance was also prepared by the reduction of tribromanilinodiketocyclopentene, $C_5Br_3(C_6H_5NH)O_2$, by shaking this compound for 10 to 12 hours with 25 per cent. alcohol saturated with sulphurous dioxide, after which the liquid was filtered and allowed to stand till all the sulphurous dioxide had escaped, when from the spontaneous evaporation yellow crystals shaped like feathers were deposited. These, after crystallization from a mixture of equal parts of benzene and

ligroin, showed the constant melting point 121°—Analysis II. It is noteworthy that no red color appeared during this reduction, even when fairly strong alcohol was used. In this respect it differed markedly from the reduction of the tetrabrom body. .

I. 0.1024 gram substance gave 0.0726 gram AgBr.

II. 0.1234 gram substance gave 0.0872 gram AgBr.

	Calculated for $C_5H_2Br(C_6H_5NH)O_2$.	Found. I.	II.
Br	30.07	30.17	30.07

Properties of Bromanilinodiketocyclopentene.—Fine yellow needles melting at 121° with decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, acetone, benzene, toluene, or glacial acetic acid; almost insoluble in cold ligroin, more soluble in hot. Strong hydrochloric acid has little effect on it; strong nitric acid or sulphuric acid forms a yellow solution, with which water gives no precipitate. Dilute nitric acid does not attack it, even when warmed on the steam bath, but if it is allowed to stand in the cold with strong nitric acid for several weeks, it is decomposed into hydrobromic and oxalic acids. Warm potassic permanganate solution produces the same effect except that the oxalic acid is burnt to carbonic dioxide. A 30 per cent. solution of hydric dioxide had no action on it even after standing for several days. Sodic hydrate dissolves it with a slight odor of phenyl isocyanide and forms a dark solution. Sodic carbonate converts it into a yellow crystalline compound described later.

A chloroform solution of the compound $C_5H_2Br(C_6H_5NH)O_2$ gave with bromine a product with the constant melting point 153°, but our analyses have not led to any probable formula, so that we are of the opinion that it is a mixture of compounds containing different amounts of bromine.

If in preparing the anilino derivative the aniline was allowed to act on the dibromdiketocyclopentene overnight instead of a few minutes, the ethereal filtrate from the hydrobromide of aniline left, on evaporation, a reddish brown amorphous substance undoubtedly analogous to that obtained by the more decided action of aniline on the tetrabrom compound.

As it was of little interest, we did not attempt its purification, which, owing to its indefinite properties, promised to be a difficult task.

Action of Sodic Carbonate on Bromanilinodiketocyclopentene.

Anilinoketotriene, $C_6H_5NHC_3HO$.—Two grams of the bromanilino body (melting at 121°) were mixed with a cold saturated solution of sodic carbonate and allowed to stand for about one week. The substance gradually dissolved, forming a brown solution and giving a faint smell of phenyl isocyanide. As time went on this solution deposited a mass of very fine yellow crystals, which were filtered out, washed thoroughly with water, and crystallized from benzene until they showed the constant melting point 221°, when they were dried *in vacuo* for analysis:

I. 0.2051 gram substance gave 0.5588 gram CO_2 and 0.0931 gram H_2O.

II. 0.2909 gram substance gave 26.01 cc. N_2 at 25° and 750.4 mm.

III. 0.1955 gram substance gave 17.10 cc. N_2 at 22° and 764.6 mm.

	Calculated for $C_6H_5NHC_3HO$.	I.	Found. II.	III.
C	74.48	74.31	....	....
H	4.83	5.07	....	....
N	9.65	....	9.84	9.98

As has been shown in the introduction, this substance is in all probability the anilinoketotriene,

$$C_6H_5NH - C \overset{CH}{<} CO.$$
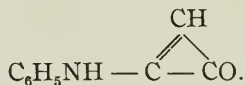
Properties of Anilinoketotriene.—It crystallizes in good-sized yellow needles, which melt sharply at 221° with decomposition. It is easily soluble in ethyl or methyl alcohol, ether, chloroform, acetone, ethyl acetate, benzene, toluene, or glacial acetic acid; essentially insoluble in ligroin or water. Solutions of the strong alkalies have no effect on it in the cold, and decompose it only slowly when warmed on the

steam bath. Strong hydrochloric acid has no visible effect upon it; strong sulphuric acid gives a purple solution with it; strong nitric acid also dissolves it with a purple color, and when warmed on the steam bath decomposes it, but the product was not studied, except to show that no oxalic acid is formed. Dilute nitric acid, under the same conditions, decomposes it with an odor of nitrobenzene. Upon extracting the liquid product with ether almost white crystals were obtained, which melted between 95° and 100° and showed no acid properties, as they did not change litmus paper or decompose carbonates. We did not have enough of this product for study. Potassic permanganate in dilute solution gave at the end of one hour an odor of phenyl isocyanide with, however, only a slight change of color; even after 24 hours the solution was not colorless, but at the end of 48 hours the color of the permanganate had disappeared entirely. The organic product was not studied. With a 30 per cent. solution of hydric dioxide a white compound was formed after several days, which was only slightly soluble in ammonic hydrate. The triene did not give metallic silver with an ammoniacal solution of argentic nitrate.

If dissolved in chloroform and mixed with a small quantity of bromine, no addition of the bromine could be observed in the first half hour; after this, however, a reaction took place, but, as part of the bromine at least undoubtedly entered the anilino group, it was hardly worth while to study the product. Phenylhydrazine gave a brown, rather tarry product, melting with decomposition at 110°, which came down in an amorphous state from all its solutions.

Action of Methyl Alcohol on Tetrabromdiketocyclopentene.

Tribrommethoxydiketocyclopentene, $C_5Br_3OCH_3O_2$.—Two grams of the tetrabromdiketocyclopentene dissolved in methyl alcohol were allowed to stand at ordinary temperatures for 4 days. At the end of this time the liquid, which gave a strong test for hydrobromic acid, was diluted with water, when a mass of very fine, nearly white, crystals was precipitated. This was filtered out and purified by crystallization from dilute

methyl alcohol until the white crystals showed the constant melting point 67°, when they were dried *in vacuo*:

I. 0.3720 gram substance gave 0.2777 gram CO_2 and 0.0325 gram H_2O.

II. 0.1368 gram substance gave 0.2141 gram AgBr.

	Calculated for $C_5Br_3OCH_3O_2$.	Found. I.	II.
C	19.83	20.36	....
H	0.82	0.98	....
Br	66.11	....	66.60

Properties of Tribrommethoxydiketocyclopentene.—It crystallizes in fine white needles melting to a colorless liquid at 67°. It is easily soluble in ethyl or methyl alcohol, ether, chloroform, acetone, benzene, or toluene; slightly soluble in hot ligroin, but essentially insoluble in cold. To judge from the appearance of a red color all these solutions show a tendency to decompose when heated, as for instance, when they are evaporated on the steam bath. Strong hydrochloric acid has no visible effect on it, but it dissolves apparently without change in strong nitric acid, or sulphuric acid. Alkalies decompose it, giving a dark-colored solution, and what seems to be a similar decomposition is brought about even by boiling it with water.

A solution of sodic carbonate in the cold slowly formed a dark solution, but this reaction was accompanied with no smell of a substituted methane. No action was observed, when a solution of the compound $C_5Br_3OCH_3O_2$ in glacial acetic acid was allowed to stand with bromine. Sulphurous dioxide with methyl alcohol and water acted upon it, giving a red solution, but the product was so tarry that we did not undertake its investigation. When an ethereal solution was mixed with aniline a red product was formed, probably identical with that obtained from the ethoxy body.

Action of Ethyl Alcohol on Tetrabromdiketocyclopentene.

Tribromethoxydiketocyclopentene, $C_5Br_3OC_2H_5O_2$.—Five grams of the tetrabromdiketocyclopentene were dissolved in 100 cc. of 95 per cent. alcohol by warming on the steam bath for a

few minutes, and the solution was allowed to stand overnight at ordinary temperatures. A large excess of water was then added and the nearly white crystalline precipitate recrystallized from a mixture of alcohol and water until it showed the constant melting point 110°, when it was dried *in vacuo* for analysis:

    I. 0.1902 gram substance gave 0.2842 gram AgBr.
    II. 0.1986 gram substance gave 0.2966 gram AgBr.

	Calculated for $C_5Br_3OC_2H_5O_2$.	I.	II.
		Found.	
Br	63.66	63.59	63.55

Properties of the Tribromethoxydiketocyclopentene.—Small, white needles which melt at 110° without decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, acetone, benzene, toluene, or glacial acetic acid; slightly soluble in ligroin when cold, more soluble when hot; insoluble in water. The best solvent for it is a mixture of alcohol and water. Strong hydrochloric acid has no visible effect on it; strong nitric acid dissolves it slightly; strong sulphuric acid dissolves it, and it is precipitated apparently unchanged by the addition of water. Aqueous sodic hydrate forms a dark solution, which does not smell of a bromine derivative of methane. A similar dark solution was obtained by heating an alcoholic solution of the ethoxy body with sodic acetate, or potassic cyanide, for 3 hours on the steam bath, but only amorphous organic products resulted. Argentic acetate also decomposed the alcoholic solution in the cold, forming argentic bromide and a brown oily product, from which no definite compound could be isolated. Plumbic nitrate and a solution in 50 per cent. alcohol on the steam bath behaved in a similar way, giving much plumbic bromide, but in this case no organic product could be found.

Action of Aniline on Tribromethoxydiketocyclopentene.— Two grams of the ethoxy compound were dissolved in ether and mixed with 2.2 cc. of aniline. After the mixture had stood a few minutes with occasional shaking, no more hydrobromide of aniline was precipitated. The solution was then filtered, evaporated to dryness, and the brown residue allowed

to stand overnight with dilute hydrochloric acid to remove the excess of aniline. After pulverization it was washed thoroughly with hydrochloric acid and water, and dried. To purify it a solution in chloroform was slowly poured, with constant stirring, into a large volume of ligroin, and after repeating this treatment several times a red amorphous product was obtained, which seemed to be free from tar, and was dried *in vacuo* for analysis:

I. 0.1393 gram substance gave 0.3109 gram CO_2, 0.0059 gram unburnt C and 0.0590 gram H_2O.

II. 0.2247 gram substance gave 14.6 cc. N_2 at 27°.2 and 759.2 mm.

	Calculated for $C_5H_2OH(C_6H_5NH)O_2$.	Found. I.	II.
C	65.03	65.10	....
H	4.43	4.71	....
N	6.90	....	7.16

What seemed to be the same product was formed by the action of aniline on the methoxy body, and of aniline, ether and alcohol on tribromanilinodiketocyclopentene, melting at 178°. A similar reaction, giving a different result, has been described already, in which aniline in alcoholic solution converted tetrabromdiketocyclopentene into the compound

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2.$$

Properties of Anilinohydroxydiketopentene.—Red amorphous powder, which melts with decomposition at 140°. Easily soluble in alcohol, methyl alcohol, ether, chloroform, or acetone; slightly soluble in benzene, toluene, or water; essentially insoluble in ligroin. Strong hydrochloric acid has no visible effect on it; strong nitric acid, or sulphuric acid, forms a dark red solution with it. Sodic hydrate dissolves it, and the solution has a strong odor of phenyl isocyanide. Phenylhydrazine seems to have no action on it.

Action of Acetic Anhydride on the Anilinohydroxydiketocyclopentene.—Three grams of the compound

$$C_5H_2OH(C_6H_5NH)O_2$$
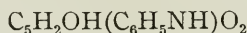
dissolved in acetic anhydride were warmed on the steam bath

for half an hour, after which the acetic anhydride was allowed to evaporate spontaneously. A chloroform solution of the residue was poured slowly, with constant stirring, into a large volume of ligroin, and after this process had been repeated several times the product was dried *in vacuo* for analysis:

0.1128 gram substance gave 5.95 cc. N_2 at 25° and 764 mm.

	Calculated for $C_5H_2OC_2H_3O(C_6H_5NH)O_2$.	Found.
N	5.71	5.92

Properties of Anilinoacetoxydiketocyclopentene, $C_5H_2OC_2H_3O(C_6H_5NH)O_2$.—An amorphous, pale brown powder, which melts with decomposition at 150°. Easily soluble in alcohol, methyl alcohol, chloroform, or acetone; moderately soluble in ether; slightly soluble in warm benzene or toluene; essentially insoluble in ligroin. Strong hydrochloric acid has no effect on it; strong nitric acid dissolves it slightly; strong sulphuric acid gives a dark green solution with it, whereas with the mother substance it gives a red solution. Sodic hydrate dissolves it with a strong odor of phenyl isocyanide. It is decomposed also by treating with water or ammonic hydrate.

Tribromtriketocyclopentene, $C_5HBr_3O_3$.—This substance was prepared by the method of Henle[1] as follows: Thirty-eight grams of crystallized sodic bromanilate were mixed with 160 cc. of water at the ordinary temperature and 12 cc. of bromine added slowly with shaking. When the evolution of carbonic dioxide had ceased, the excess of bromine was removed with acid sodic sulphite. Fifty grams of 30 per cent. sulphuric acid and 100 grams of sodic sulphate were then added and the solution extracted three times with 150 cc. of ether. Upon cooling the oily residue from the ether with ice water it solidified in small crystals, which were washed with benzene and crystallized from chloroform, when they showed the correct melting point, 191°.

Tetrabromdiketocyclopentene, $C_5Br_4O_2$.—Six and eight-tenths grams of the tribromtriketocyclopentene were warmed with phosphoric pentabromide according to Henle's directions,

[1] Ann. Chem. (Liebig), **352**, 45 (1907).

in an open dish on the steam bath, until the evolution of hydrobromic acid had ceased, when the product was poured upon ice, and then water added, and the mixture warmed to destroy the phosphoric oxybromide. The brown mass thus obtained was dissolved in strong nitric acid and precipitated with water, when yellow crystals were obtained which, after crystallization from benzene and ligroin, melted at 142°. To prove that the substance made in this way is identical with our product from tetrabromorthoquinone, it was converted into the methoxy derivative, which melted at 67°, and the ethoxy compound, which melted at 110°, showing that they were the same as the corresponding derivatives of our substance.

CAMBRIDGE, September 24, 1909.

STUDIES IN THE PREPARATION OF NITRILES.
BY E. EMMET REID.

In making a quantity of benzonitrile from benzoic acid and lead sulphocyanate according to the method of Letts and Krüss, some observations were made which led to considerable improvement in the yield obtainable and also to views, quite different from theirs, as to the mechanism of the reaction.

Historical.

In 1872 E. A. Letts,[1] of London, studied the action of potassium sulphocyanate on acids, using, particularly, a mixture of 180 grams (three molecules) of acetic acid to 100 grams (one molecule) of the salt, and boiling the mixture several hours. He found the main products to be acetamide and carbon oxysulphide. Some hydrogen sulphide and carbon dioxide were also found, but these he supposed to be due to a secondary reaction. He represented the reactions thus:

(1) $HCNS + C_2H_3OOH = C_2H_3ONH_2 + COS,$

and

(2) $C_2H_3ONH_2 + COS = CH_3CN + CO_2 + H_2S.$
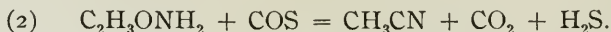
In case of acetic acid he did not identify the nitrile, but with

[1] Ber. d. chem. Ges., **5,** 669–74.

isobutyric acid and valeric acid he found both amide and nitrile, the amide being the main product.

With benzoic acid the nitrile was almost the sole product, only traces of the amide being found. In this case he represented the reaction by the equation

(3) $HCNS + C_7H_5OOH = C_7H_5N + CO_2 + H_2S.$

He actually used two molecules of benzoic acid to one molecule of potassium sulphocyanate, as one molecule of the acid was used up in setting free the sulphocyanic acid. Half of the benzoic acid was recovered from the residue. He reported the yield as 80 per cent. of the acid used up, or 40 per cent. of the total benzoic acid taken.

Pfankuch[1] heated barium benzoate with excess of barium sulphocyanate and got benzonitrile but mixed with large quantities of other products. Barium acetate and barium sulphocyanate gave similar results but the other products were in excess of the acetonitrile. Most of his effort was spent on the identification of the products other than the nitriles.

Kekulé[2] took up the question. He quotes Williams, who had repeated the work of Letts and of Pfankuch. This worker obtained smaller yields of nitriles than Letts reported, while Pfankuch's results were not entirely verified. Kekulé mentions work of Purper who heated benzoic acid with ammonium sulphocyanate and got benzamide. Kekulé recalls the fact that Letts had gotten amides from acids of the fatty series, but nitriles from benzoic and cinnamic acids, and asks why the reaction is different in the two series and also why ammonium and potassium salts react differently. He states the case thus: "The first molecule of acid gives sulphocyanic acid, which reacts with the second molecule of the organic acid, or on the ammonium salt of the acid, if ammonium sulphocyanate is used, so that acetamide and carbon oxysulphide are formed by double decomposition. Since, as was shown above, 1 molecule of ammonium sulphocyanate can change only 1 molecule of benzoic acid into amide, so it is

[1] J. prakt. Chem., [2] 6, 97.
[2] Ber. d. chem. Ges., 6, 111–4.

proved that, at least under these conditions, carbon oxy-sulphide does not act dehydratingly on ammonium benzoate to form benzamide. If, as Letts found, in the distillation of potassium sulphocyanate with 2 molecules of benzoic acid, nitrile is formed, this can result only from the dehydrating effect of potassium benzoate on benzamide, whereby the nitrile is formed. A special experiment, in which 12 grams benzamide were distilled with 17 grams potassium benzoate and yielded 8 grams benzonitrile, proved the correctness of this view." Müller found that on rapid distillation the amide was obtained. Kekulé thought that the amides of the fatty series were more difficult to dehydrate by the corresponding potassium salts than were the aromatic amides.

G. Krüss[1] complained of the yield in Letts' process and improved the method by substituting lead sulphocyanate for the potassium salt. His idea was that the hydrogen sulphide first evolved would act with the unchanged lead sulphocyanate to free the sulphocyanic acid, and less of the benzoic acid would be required for this purpose. Lead sulphide instead of the benzoate would be left in the retort and all of the benzoic acid put in might take part in the nitrile formation. "On account of the instability of lead sulphocyanate, at high temperatures, an excess was always used." He gives no intimation as to how much excess he used. Schöpff,[2] in making brombenzonitriles, used over twice as much of the lead sulphocyanate as is called for by the equation. Krüss reports yields of 50 to 55 grams benzonitrile from 100 grams of benzoic acid, or double what he was able to obtain by the method of Letts. He gives the equation

(4) $2C_6H_5COOH + Pb(CNS)_2 = 2C_6H_5CN + PbS + H_2S + 2CO_2.$
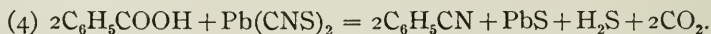
Tingle[3] made a comparative study of this and other methods of preparation of benzonitrile with reference to the cost of materials and time required.

General and Theoretical.

In making a quantity of benzonitrile according to the

[1] Ber. d. chem. Ges., **17**, 1760–9.
[2] *Ibid.*, **23**, 3435–40.
[3] This Journal, **35**, 87.

method of Krüss the yield was not found satisfactory. In one experiment the gas evolved was passed through lead acetate solution and the precipitate obtained appeared insignificant compared with the amounts of reagents in the retort. This led to the following quantitative experiment:

Into a small distilling bulb the outlet of which entered a small U-tube standing in a beaker of cold water were weighed, 4.884 grams of benzoic acid and 6.466 grams lead sulphocyanate. The gas issuing from the other side of the U-tube was passed through a large and a small flask of acidulated lead acetate solution and then through a large and a small flask of barium hydroxide solution, the latter being protected by a wash bottle of caustic soda. During the experiment purified air was slowly aspirated through the whole system. The tube which admitted the air to the reaction flask reached nearly to the surface of the mixture. The flask was heated in a bath. At 197° the reaction had begun. During 30 minutes the temperature was raised gradually to 226°. At the end of this time there seemed to be no further action. The nitrile obtained weighed 1.476 grams, or 36 per cent. of the calculated amount. The lead sulphide collected from the two flasks weighed 0.033 gram, corresponding to 0.0047 gram hydrogen sulphide, or 0.68 per cent. of the theoretical. The barium carbonate weighed 3.432 grams, corresponding to 0.765 gram carbon dioxide, or 43 per cent. of the calculated.

The fact that such a small amount of hydrogen sulphide was evolved suggested that it might in some way be involved in the formation of complex products. High-boiling products had been noticed by Pfankuch.[1] Williams had obtained products boiling at 220°–245° and 245°–275°. In order to avoid the formation of hydrogen sulphide, lead benzoate was substituted for the benzoic acid. Pfankuch and Williams[2] had both used a mixture of salts, but had used barium benzoate and barium sulphocyanate, with the latter in large excess. Their results were poor as regards the yield of nitrile. Experi-

[1] J. prakt. Chem., [2] 6, 97.
[2] Ber. d. chem. Ges., 6, 111–4.

ment proved that the mixture of lead benzoate and lead sulphocyanate did give a satisfactory yield of benzonitrile.

While little is known of the mechanism of such pyrogenetic reactions, yet it is interesting to compare this with several other reactions which take place under similar circumstances with more or less similar substances. For convenience, a mixture of salts is written as a mixed salt.

A hydrocarbon is formed from a salt of a carboxy acid and lime,

$$Ca\begin{cases} CO_2 C_6H_5 \\ O H \end{cases} = CaCO_3 + C_6H_5.H.$$
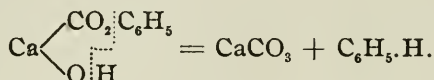
A ketone is formed from a salt of a carboxy acid,

$$Ca\begin{cases} CO_2 C_6H_5 \\ O COC_6H_5 \end{cases} = CaCO_3 + C_6H_5COC_6H_5.$$
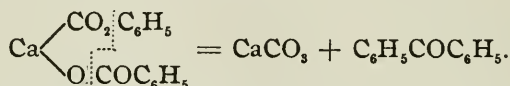
An aldehyde is formed from a carboxy salt and a formate,

$$Ca\begin{cases} CO_2 C_6H_5 \\ O CHO \end{cases} = CaCO_3 + C_6H_5.CHO.$$
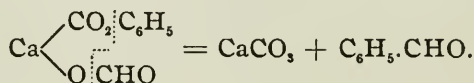
Since lead benzoate and lead sulphocyanate give the nitrile under the same conditions it seems not amiss to write the reaction in the same way, remembering, however, that the thiocarbonate would break up.

$$Pb\begin{cases} CO_2 C_6H_5 \\ S CN \end{cases} = PbS + CO_2 + C_6H_5.CN.$$
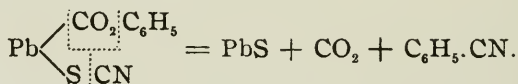
This equation suggested the possibility of getting a similar reaction with the cyanate in place of the sulphocyanate. This was found to work:

$$Pb\begin{cases} CO_2 C_6H_5 \\ O CN \end{cases} = PbCO_3 + C_6H_5.CN.$$
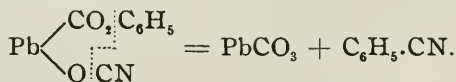
The fact that sulphocyanates are formed from cyanides by the addition of sulphur suggested the idea of using a cyanide and sulphur in place of the sulphocyanate. This was found to work well, but whether the sulphocyanate is formed as an

intermediate product or not has not been found out. It may be represented simply in this way:

$$S + Pb \begin{cases} CO_2.C_6H_5 \\ ----- \\ CN \end{cases} = PbS + CO_2 + C_6H_5.CN.$$
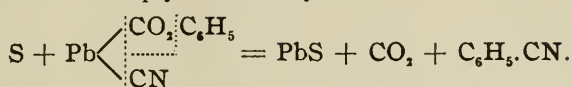
The fact that a nitrile is formed from a sulphonate and a cyanide on fusion,

$$Ca \begin{cases} SO_3.C_6H_5 \\ ----- \\ CN \end{cases} = CaSO_3 + C_6H_5.CN,$$
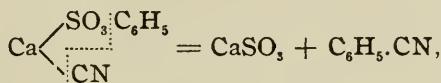
suggested that a nitrile might be formed also from a carboxy salt and a cyanide in the same manner. Experiment has shown that some nitrile and carbon monoxide are formed, but the amount and apparent complexity of the by-products of the reaction indicate that it is not as simple as the following equation would indicate:

$$Pb \begin{cases} CO_2.C_6H_5 \\ ----- \\ CN \end{cases} = PbO + CO + C_6H_5.CN.$$
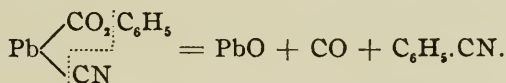
Lead, sodium, zinc, and barium benzoates have been studied with potassium cyanate, lead cyanate, potassium sulphocyanate, lead sulphocyanate, barium sulphocyanate, lead cyanide and sulphur, lead ferrocyanide and sulphur, zinc ferrocyanide and sulphur, potassium ferrocyanide and sulphur, silver cyanide and sulphur, and lead ferrocyanide without sulphur.

All of the combinations of the above which have been tried have given considerable yields of nitriles, the amount of the yield varying with circumstances. The yield is doubtless mainly dependent on the melting point of the compounds and the temperature at which they decompose. High-melting compounds may be largely decomposed before they come into efficient contact with the other reagents. A high reaction temperature favors side reactions. Salts of weak bases may be partly decomposed while being dehydrated previous to use, or may be decomposed by water present during the reaction itself. The cyanates did not give good yields, apparently for the reason that the oxygen of the cyanate caused the combustion of some of the organic acid.

Those who have worked on this reaction have supposed that it took place solely between the molecules of the two acids in the free state. Since the benzoic acid would form lead benzoate with a portion of the lead sulphocyanate, the two salts would be present during the reaction as well as the two acids. Hence the results of previous workers may be interpreted just as well on the assumption that the reaction takes place between the salts. The results of the present experiments, in which only salts were present, can be explained in only the one way, namely, that the reaction takes place between the salts. The fact that, in the method of Krüss, one-half of the lead sulphocyanate was needed to form lead benzoate with which the other half of the sulphocyanate was to react explains why the yields were about 50 per cent. Krüss and those who have used his method have sometimes brought the yield somewhat above 50 per cent. by using an excess of the sulphocyanate. Tingle used two equivalents of lead sulphocyanate to one equivalent of benzoic acid. Since free sulphocyanic acid is extremely unstable at high temperatures it would be driven out almost quantitatively by the benzoic acid till there would be in the retort a mixture of equivalent quantities of lead benzoate and lead sulphocyanate. This is just the mixture which was put into the retort in some of the present experiments. The yield of 71 per cent., recorded by Tingle from his mixture, agrees well with that here obtained from a mixture of the salts. The presence of a large excess of the lead sulphocyanate makes the mass more difficult to fuse and seems to favor side reactions.

Several substituted benzoic acids have been tried. The three aminobenzoic acids gave only small quantities of distillates which, on account of their apparent complexity, seemed not worth working up. Aniline was proved to be present in considerable quantity in the case of the ortho compound. *p*-Nitrobenzoic acid was tried in the form of its lead salt with lead sulphocyanate, but exploded on heating. Meta- and parabrombenzoic acids gave good results. There seems to be every reason to think that the method as given below would be readily applicable to a number of the aromatic acids.

Some work has been done on acids of the fatty series and it is certain that the reaction takes place in much the same way but the detailed study of the conditions, yields, etc., must be left for another paper.

Experimental.

Materials.—Though all of the materials used have been made and described long ago, the scarcity of information concerning some of them warrants the insertion of some details.

The most of the lead benzoate used was made by precipitation. Benzoic acid was dissolved in water with the addition of ammonia or caustic soda to exact neutrality and to this was added a solution of the calculated amount of lead nitrate. The solutions must not be hot, though they may be warm, since in hot water the lead benzoate partially melts or masses together into a sort of dough. The precipitate was filtered and well washed. It is so nearly insoluble in water that the mother liquors may be thrown away and the salt thoroughly washed. The air-dry salt was dehydrated in a porcelain dish over a free flame. It must be stirred constantly. At about 100° it gets pasty and begins to give off water. At higher temperatures it softens more and more and continues to give off water. At 150° the most of the water is gone and the salt is thoroughly liquid. It was usually heated to about 210°. It was then poured out on a slate table and subsequently powdered. The fused salt forms a perfectly transparent, more or less amber colored, brittle mass.

The same salt was also made by direct fusion of benzoic acid and lead oxide. For this purpose the acid was melted in a dish and the calculated amount of lead oxide sifted in with constant stirring. The mass was stirred constantly and the temperature gradually raised to about 210°. A few particles of metallic lead are formed and the color of the fused mass is somewhat darker than that made in the other way. This is a very rapid and convenient way of making the salt. The product, when powdered, is practically white. The salt made in this way was used in experiments 8, 9, 11, and 12.

Whichever method is used, the dehydrated salt probably

still contains some water and has certainly lost some benzoic acid. In the calculation of yields, however, it was considered as having the theoretical composition.

Zinc benzoate, recently studied by Parietta,[1] can not be made by the fusion method as its melting point is too high. When made by precipitation a considerable amount, about 14.5 grams per liter at 59°, remains in the solution. The precipitated salt is best filtered hot. It is anhydrous and may be dried at 200° in an air bath without softening or caking together.

Barium and sodium benzoates were made by direct neutralization and evaporation. Both were dried at high temperatures.

Liebig made lead sulphocyanide and described it as "yellow crystals." It was made by precipitation from fairly dilute, moderately warm, neutral solutions of equivalent quantities of ammonium sulphocyanate and lead nitrate. In one preparation specially pure salts were used and the product was washed with water, alcohol, and ether. It dried rapidly and remained a pure white, except that when it was exposed to light it turned a little dark on the surface. The bulk of the salt used in this work was decidedly yellow after drying and standing some time. The salt is anhydrous and may be dried at 140° without appreciable decomposition.

The lead and zinc ferrocyanides and the lead and silver cyanides were made by precipitation from neutral solutions. The lead ferrocyanide proved difficult to dehydrate. It lost water only slowly at 160°. It was heated to 200° for eight hours in a Kjeldahl flask, the neck of which slanted down and projected from the air bath. Access of air was nearly cut off by a stopper carrying a tube. The salt takes fire at about this temperature when heated in open air. The zinc ferrocyanide was dehydrated in the same way.

Method of Work.—The dry powders were well mixed and put into a plain retort. The neck of the retort was connected with a half-inch tube about two and a half feet long which

[1] Gaz. Chim. Ital., 36, II, 67–70.

reached nearly to the bottom of a flask, one-half to one liter in size. In the later experiments a plug of cotton was put in the neck of this flask to aid in retaining the fumes, and the gases were led into a second empty flask. In this way a few drops of nitrile were found in the second flask. For an amount of salts equivalent to 122 grams of benzoic acid a 250 cc. retort was used. Smaller retorts were used with the smaller amounts of materials. The retort may be nearly filled with the dry mixture. In no case was much trouble caused by foaming, though the burner was held in the hand and, during the first part of the reaction, the heat was applied to the side of the retort so as to keep the reaction under control. The time of heating was from thirty minutes to a little over an hour. A single Bunsen burner was used except that sometimes an extra large burner was used to finish the reaction. When the heat is applied the mass melts and bubbles of gas and fumes begin to come off at once. In some experiments the nitrile began to drop from the end of the retort neck within two minutes after the flame was applied. The reaction usually proceeds regularly and spreads through the whole mass which becomes more or less liquid throughout. At the end the residue melts down into a cake and the nitrile ceases to come off.

Method of Examination.—The methods of separation of the constituents of the crude distillate were only such as are used in ordinary organic preparations. The aim has been to find and report such quantities as might readily be obtained with the simplest possible apparatus and the least outlay for time and chemicals. The question has not been so much what amount of nitrile is formed in a given reaction, but what amount can be simply and profitably obtained by such reaction.

The distillate from the retort was treated with an equal volume of water and enough ammonia to cause it to smell of the gas. This mixture was distilled with steam. For mixtures yielding 40 to 75 grams of nitrile a flask from 700 to 1000 cc. in size was used as a receiver. A handful of salt was put into the flask with enough water to wet it. The distillate

was caught in this till the flask was three-fourths or more full. The mixture was shaken to dissolve the bulk of the salt and then brine poured in till the nitrile was driven up into the neck of the flask. After standing a while in a cool place the nitrile was pipetted off and weighed. The last small portion of nitrile in the neck of the flask was diluted with a little ether and removed. This was warmed in a beaker to expel the ether and to the main portion. In some of the later experiments the added contents of the flask were extracted with ether. In a special experiment 65.9 grams of benzonitrile were distilled with steam and recovered in this manner; found, 62.8 grams, showing a loss of 3.1 grams. On the other hand the nitrile was not dried before weighing. This error partially balanced the other.

The residue in the flask after the steam distillation was filtered hot and what was left on the funnel was set down as "tar." Benzophenone was sought for in this tar but was not found. Usually long needles separated from this filtrate on cooling. These were sometimes an inch or so in length and of a pale yellow color and silky appearance. These varied in appearance and color but were usually of this description. They are put down in the results as "needles." Specimens of these needles have since been treated with strong caustic soda solution. This separates them into two compounds, one of which is not soluble in caustic soda and the other of which is precipitated from its caustic soda solution by the addition of ammonium chloride. For the present, these are designated as compounds A and B.

Compound A.—This is insoluble in caustic soda, melts at 138°, dissolves in 140 parts of boiling water, and separates from such solution in perfectly white needles, often an inch in length. Sometimes it has been obtained in pearly white scales with the same melting point. It distils near 280°, is slightly volatile with steam, and gives ammonia when heated with strong alkali.

Compound B.—This is a very weak acid as it dissolves in strong caustic soda but not in ammonium hydroxide. It is soluble in 230 parts of boiling water and separates from this

solution in long slightly straw-colored needles. It melts at 230° and gives ammonia when heated with strong alkali.

These two compounds are still under investigation.

The filtrate from these needles was acidified to obtain the benzoic acid. Ammonium benzoate loses a small part of its acid on distillation with steam. In a special experiment 1.7 grams out of 35 grams were lost in this way. Beginning with experiment 11, the original crude product was, in most cases, extracted with soda solution to obtain the acid.

The results are collected below in tabular form, the experiments being given in practically the same order in which they were made. The later ones are more trustworthy. All weighings were made on a balance barely sensitive to 0.1 gram.

The yield of benzonitrile is calculated on the total benzoic acid supposed to be in the salt used. In cases in which much of the acid was recovered the "net" yield of nitrile is also calculated. This is based on the amount of benzoic acid which disappeared during the reaction. The yields found are supposed to be considerably less than the amounts formed.

Where two numbers are given under the heading "time" the lower figures give the time during which the retort was heated with an extra large burner after it had been heated with the ordinary burner for the time given by the upper figures.

The figures in the first column, under the formulae of the constituents of the mixture, represent the weights used in grams. Under these are placed the gram-equivalents of the substances used.

No.	Composition of mixture.	Time in min.	Crude prod.	Nitrile. Calc.	Nitrile. Found.	Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
1	$K_4Fe(CN)_6$, 15 S, 8 0.8 $Pb(C_6H_5CO_2)_2$, 62.3	....	18.6	25.7	12.1	....	....	....	47	....
2	$Pb(CN)_2$, 105 S, 26 0.8 $Pb(C_6H_5CO_2)_2$, 180	....	47	82.4	12.5	....	5	8	15	....
3	$Pb_2Fe(CN)_6$, 110 S, 33 1.1 $Pb(C_6H_5CO_2)_2$, 212 0.8	60	98	98	63.3	1	1.5	16	64	75
4	$Pb_2Fe(CN)_6 \cdot 3H_2O$, 59.3 S, 18 0.55 $Pb(C_6H_5CO_2)_2$, 107 1	30	51.8	49.2	24.6	0.5	2.0	17.5	50	71
5	KCNO, 20 0.55 0.25 $Pb(C_6H_5CO_2)_2$, 62.3	....	13	25.7	....	....	....	....	low	....
6	$Pb(CNO)_2$, 32.5 0.23 0.26 $Pb(C_6H_5CO_2)_2$, 59.3	....	13	23.2	11.1	....	....	0.0	48	....
7	$Pb(CNS)_2$, 153 0.95 $Pb(C_6H_5CO_2)_2$, 212	30	82	97	60	0.0	3	7.0	62	66
8	$Pb(CNS)_2$, 150 0.88 0.95 $Pb(C_6H_5CO_2)_2$, 150	58	65	69	46.3	....	....	7.0	68	74
9	$Pb_2Fe(CN)_6$, 114.6 1.08 S, 33 1.03 $Pb(C_6H_5CO_2)_2$, 212 0.95	....	90	97	66	~3	1	15.0	68	78

No.	Composition of mixture.	Time in min.	Crude prod.	Nitrile. Calc.	Found.	Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
10	AgCN, 25.2 0.19; S, 15 0.5; $Pb(C_6H_5CO_2)_2$, 42 0.18	30	23.5	19.3	10.2	...	...	5.5	53	70
11	$Pb_2Fe(CN)_6$, 90 0.88; S, 28 0.88; $Pb(C_6H_5CO_2)_2$, 180 0.80	70	71.6	82.4	48.3	1.3	1.3	9.3	58.6	65
12	$Pb_2Fe(CN)_6$, 104.3 0.8; S, 32 0.8; $Pb(C_6H_5CO_2)_2$, 179.6 0.8	45	78.5	82.4	49.8	7.5	...	9.6	60	66
13	$Pb_2Fe(CN)_6$, 91 0.88; S, 28 0.88; $Pb(C_6H_5CO_2)_2$, 180 0.80	23 7	78.6	82.4	52.6	2.1	...	13.3	64	74
14	$Pb(CNS)_2$, 161.5 1.0; $NaC_6H_5CO_2$, 115.2 0.8	31 20	58.3	82.4	47.0	0.0	...	0.5	57	....
15	$Pb(CNS)_2$, 161.5 1.0; PbO, 25 0.23; $Pb(C_7H_5O_2)_2$, 179.6 0.8	41	79.9	82.4	53.3	...	...	9.0	65	75
16	$Zn_2Fe(CN)_6$, 50.2 0.88; S, 28 0.88; $Pb(C_7H_5O_2)_2$, 179.6 0.80	33 8	84.9	82.4	47.5	0.7	1.7	23.2	57	80
17	$Pb(CNS)_2$, 161.5 1.0; $Zn(C_7H_5O_2)_2$, 122.8 0.8	30 6	77.0	82.4	....	0.5	2.5	6.3	86	91

No.	Composition of mixture.		Time in min.	Crude prod.	Nitrile.		Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
					Calc.	Found.					
18	$Pb_2Fe(CN)_6$, 80 0.77	S, 28 0.88 $Zn(C_7H_5O_2)_2$, 107.5 0.7	25 8	69.5	72.1	44.5	5.0	3.0	10.6	65	74
19	$Pb_2Fe(CN)_6$, 67.8 0.65	$Pb(C_7H_5O_2)_2$, 145.9 0.65	24 4	53.6	67	43.9	1.0	3.5	1.0	62.5	...
20	$Pb(CNS)_2$, 113.0 0.7	$Zn(C_7H_5O_2)_2$, 107.6 0.7	25 12	66.9	72.1	54.4	0.5	1.6	4.0	75.4	79
21	$Ba(CNS)_2$, 101.4 0.8	$Ba(C_7H_5O_2)_2$, 151.8 0.8	22 28	60	82.4	48.9	...	7.9	0.0	59	...
22	$Pb_2Fe(CN)_6$, 66.8 0.64	$Zn(C_7H_5O_2)_2$, 98.3 0.64	54 14	35.1	66	22	...	...	...	33	...

Remarks on the Experiments.

Experiment 4.—This was made to test the effect of the presence of water in the mixture. The lead ferrocyanide, which contains 3 molecules of water, was used in air-dry condition. The yield is cut down considerably.

Experiment 5.—Unusually high temperature required and charred residue left in the retort. Free ammonia in the distillate.

Experiment 10.—Since silver cyanide frequently gives isocyanides and has been thought to have the constitution Ag-NC, the purpose of this experiment was to find whether it would yield such a product in this reaction. On account of the known instability of phenyl isocyanide at high temperatures and of its known tendency to combine with sulphur, an extra amount of sulphur was put in so as to form phenyl mustard oil in case the isocyanide were present at any time during the reaction. On distillation of the 10.2 grams of nitrile obtained in this experiment, 1.5 grams went over below 185° and 7.7 grams between 185° and 212°. The remainder, about one gram, was mixed with aniline, warmed, and stirred, but no formation of thiocarbanilide was observed. With fuming nitric acid it gave no test for sulphur.

Experiment 11.—In this the amount and nature of the gases evolved were studied also. From the usual receiver the gases were passed through acidified lead acetate and then through three flasks of strong caustic potash solution, then into an aspirator bottle which was full of water at the beginning of the experiment; 1800 cc. of gas were obtained. As practically all of this was collected during the first part of the experiment when the air was being driven out of the apparatus and as the amount corresponds quite well with the volume of the retort and receivers which were left full of carbon dioxide instead of the air which they originally contained, it is evident that only carbon dioxide was given off. No hydrogen sulphide was found. The carbon dioxide found was 24.2 grams, or 68.8 per cent. of the calculated.

Experiment 12.—The carbon dioxide was weighed in this also and was found to be 79.7 per cent. of that calculated on

the total benzoic acid supposed to be in the retort, but in this experiment 10 per cent. of the acid was recovered. Hence the carbon dioxide found was 88.5 per cent. of that calculated from the benzoic acid actually taking part in the reaction.

Experiment 16.—This was to test the suitability of zinc ferrocyanide for use in place of lead ferrocyanide. While the net yield is raised, there is no improvement on the whole.

Experiments 17 and 18.—These were made to compare zinc benzoate with lead benzoate. There is a marked improvement in the yield. These two experiments show the best method for making benzonitrile. On account of the greater ease in obtaining lead sulphocyanate in the dry condition as compared with the ferrocyanide, experiment 17 represents the best laboratory method. For factory use the cheapness of the ferrocyanides may give the preference to the method of experiment 18. The retort was unharmed in both experiments.

Experiment 20.—This, as compared with No. 17, shows that a slight excess of the lead sulphocyanate is desirable.

Experiments 19 and 22.—These were made to test the utility of the sulphur commonly added. They show that the addition of the sulphur to the ferrocyanides is a decided advantage. The yields are better with the sulphur and the reactions take place at more moderate temperatures and go more smoothly.

Experiment 21.—This was made to test the salts used by Pfankuch. An extremely high temperature is required. The retort was thoroughly blistered and a large amount of tarry products was formed. The difficulty seems to be in the high melting points of the barium salts. A considerable amount of free ammonia was in the distillate. The nitrile obtained by the usual steam distillation was slightly fluorescent and, on fractionation, gave an unusually large amount, 15 per cent., of liquid boiling above 192°.

Experiment 22.—In this case the carbon dioxide produced was weighed and found to be 24 grams out of a possible 28 grams. The remaining gas contained 1 or 2 grams of carbon monoxide. So far there is no way of deciding whether carbon dioxide results from the oxidation of carbon monoxide originally

produced according to the equation given above, or whether the carbon dioxide is the original product. A highly complex mass was left in the retort.

The Benzonitrile Produced.—The products of experiment 11 to 20 were fractionated separately. On the first distillation, on the average, 16 per cent. went over below 186° and 75 per cent. between 186° and 192°, leaving 8 per cent. of residue. Further examination showed that the lower fractions were benzonitrile containing a little alcohol and ether. The residues above 192° proved to be mainly benzonitrile mixed with a small quantity of tarry products and a little of compound A mentioned above.

On refractionating the residues from 870 grams of crude nitrile, 26 grams of product boiling above 192° was obtained. From the 6 gram fraction of this boiling between 275 and 300°, 1.65 grams of compound A was obtained by drying the pasty mass on a porous plate.

Substituted Benzoic Acids.

As noted above, the three aminobenzoic acids do not give nitriles according to this method. The nitrobenzoic acids give explosions. Salicylic acid and phthalic acids give complicated products. All of these present special difficulties.

Lead *m*-brombenzoate (27.5 grams) was distilled with 20 grams (1.33 equivalents) lead sulphocyanate. The crude product weighed 13.0 grams, from which 1.2 grams of the acid was recovered. The remainder was distilled with steam and yielded 9.25 grams of the nitrile in good condition. This is 60 per cent. of the calculated.

Similar yields were obtained with lead *p*-brombenzoate, whether distilled with lead sulphocyanate or with lead ferrocyanide and sulphur. The distillation of *p*-brombenzonitrile with steam was found to be tedious and wasteful. Recrystallization from alcohol gave a purer product with less loss. Schöpff used over two equivalents of lead sulphocyanate in making the brombenzonitriles by the method of Krüss and reported 45 and 33 per cent. yields, respectively, for the meta and para nitriles.

Preparation of Benzonitrile.

As a laboratory method of preparing benzonitrile the following is suggested: To a hot solution of 50 grams of caustic soda in 400 cc. of water, 150 grams of benzoic acid are added. The solution is carefully neutralized by the addition of ammonia or soda solution. One hundred and eighty grams of zinc sulphate are dissolved in 400 cc. of hot water. The two solutions are well mixed and the precipitated zinc benzoate filtered off hot. This is washed several times and spread out on a paper to dry. When air-dry it is heated to 200° for several hours in an air bath. The mother liquor from the zinc benzoate may be concentrated and acidified for the recovery of some of the benzoic acid.

One hundred and seventy-five grams lead nitrate (or 200 grams lead acetate) are dissolved in 500 cc. warm water and 80 grams of ammonium sulphocyanate are likewise dissolved in 500 cc. water, and the two solutions mixed. The precipitated lead sulphocyanate is washed well with water and then twice with alcohol. It is spread on paper to dry. When air-dry, it may be further dried by heating for several hours from 120° to 140°.

To 120 grams of the dried zinc benzoate are added 160 grams of the lead sulphocyanate. The two are thoroughly mixed by grinding together in a mortar. The mixture is put into a 250 cc. plain retort which is connected by an air condenser with a dry one-liter flask. The retort is heated with a Bunsen burner held in the hand. The heat is applied first at the side of the retort, one portion being heated at a time. Sufficient heat should be applied to keep the reaction going well though care must be taken to avoid foaming over. When the reaction gets slow more heat is applied. An extra burner may be used. The retort is heated as long as any liquid goes over. A high temperature is required towards the end. The retort may be cleaned with nitric acid.

The nitrile is obtained from the distillate by treating with ammonia, distilling with steam and salting out as described above.

Conclusions.

1. The best laboratory method for the preparation of ben-zonitrile is to distil dry zinc benzoate with dry lead sulphocyanate.

2. A mixture of equivalent quantities of lead ferrocyanide and sulphur may be used in place of the sulphocyanate.

3. The formation of benzonitrile under these conditions takes place substantially according to the following equation:

$$Pb\begin{cases} CO_2C_6H_5 \\ SCN \end{cases} = PbS + CO_2 + C_6H_5CN.$$
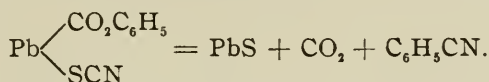
4. Ferrocyanides may sometimes in organic synthesis be substituted for cyanides.

It is desired to reserve the study of this reaction in the fatty series for further work.

JOHNS HOPKINS UNIVERSITY.

OBITUARIES.

LUDWIG MOND.

By the death, in London, on December 11, 1909, of Dr. Ludwig Mond, chemistry lost one to whom she will ever be indebted, for not only by his personal talent and labor, but also by generous and unstinted use of his large fortune, he has contributed largely to the advance of the science. The "International Catalogue of Scientific Literature" and the Davy-Faraday Laboratory are enduring monuments to his memory, and his benefactions to other institutions and even individuals are numberless.

Born in Cassel on March 7, 1839, Mond received his preparatory instruction in the schools of that city. He then went to Marburg, where he studied under Kolbe, and from there to Heidelberg to pursue his studies in Bunsen's laboratory. After graduating, he at once turned his attention to technology and for four years was connected with different German and Dutch factories, sometimes as analyst, sometimes as director. In 1862, having developed and patented a process for recovering the sulphur from the alkali-waste obtained as by-product in the manufacture of soda by the LeBlanc method, he went to

England to introduce his process in the great alkali works of that country. It was adopted by several manufacturers and Mond, after erecting and for a short time managing a LeBlanc soda factory in Holland, returned to England and settled down to the business of making alkali.

In the meantime the Solvay brothers had worked out their ammonia-soda process, and Mond was so impressed by its possibilities that he determined to risk his little capital in securing a license to work it in England. With the coöperation of Mr. (now Sir) John T. Brunner, under the firm name of Brunner, Mond & Co., a factory was erected at Winnington in Norwich which was destined to become one of the largest of its kind in the world, until it now employs 4000 men. Its great success was in large measure due to Mond. He displayed great skill in overcoming difficulties and introducing improvements, such as increasing the efficiency of the coal used as fuel by the formation of Mond gas and the recovery of the nitrogen as ammonia. In this connection he was led to investigate the action of carbon monoxide on metals, which resulted in the discovery of the metallic carbonyls and of a new process of extracting nickel from its ores, which is now widely used. The occlusion of gases by the platinum metals also engaged his attention.

Besides endowing the Davy-Faraday Institute, he made liberal donations to the Royal Institution, Cambridge, Liverpool and Manchester Universitie, University College, London, and the Lister Institute. Being compelled, in the last 20 years, through ill health, to spend his winters in Rome, he became interested in the chemical institute of the University there, an interest of which he gave very material proofs. An intimate friend of Canizzaro, he last year founded a prize bearing that scientist's name, and in the same year contributed munificently to the establishment of the Chemische Reichsanstalt.

He was deeply interested in art, and his collection of paintings, accumulated during his visits in Italy, is one of the most valuable in England.

His merits as a scientist were widely recognized: he held honorary degrees from many universities, was a Fellow of various scientific societies, president of the Society of Chemical Industry in 1888–1889 and of the chemical section of the British Association in 1896. He was recently offered the presidency of the Chemical Society but was compelled to refuse the honor on account of ill health.

CHARLES BENJAMIN DUDLEY.

Dr. Charles Benjamin Dudley, chief chemist of the Pennsylvania Railroad Company, died at his home in Altoona on December 21, 1909.

A short account of Dr. Dudley's life and of the services he has rendered to chemistry and technology will be published in the next number of THIS JOURNAL.

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REVIEWS.

THE GENERAL CHARACTERS OF THE PROTEINS. BY S. B. SCHRYVER, PH.D., D.SC., Lecturer on Physiological Chemistry, University College, London. London, New York, Bombay and Calcutta: Longmans, Green and Co. 1909. pp. x + 86.

This book appears to be carefully compiled but the fact that the majority of the subjects discussed do not lend themselves to more than a superficially exact treatment naturally detracts from the interest of the work. It may well be, however, that a clear exposition of the obvious deficiencies in our store of facts may stimulate further research. The subject matter is divided into sections on the general, physical and chemical properties of the proteins, together with a short account of the newly developed biological methods for the identification and differentiation of proteins. Each of the essays is provided with a useful bibliography.　　　　　　　　　H. D. DAKIN.

OUTLINES OF PHYSICAL CHEMISTRY. BY GEORGE SENTER, PH.D., B.SC., (Lond.). London: Menthuen & Co. 1909. pp. xvii + 369. Price, 3s. 6d.

The purpose of the author may be gathered from his statement in the preface: "I have preferred to deal in considerable detail with those branches of the subject which usually present most difficulty to beginners, such as the modern theory of solutions, the principles of chemical equilibrium, electrical conductivity and electromotive force, and have devoted relatively less space to the relationships between physical properties and chemical composition." There are frequent references to the literature, and the various sections are closed by excellent "practical illustrations." The presentation is exceptionally clear. The author rides no particular hobby, so that the viewpoint is orthodox and thus calculated to fit the need of the average teacher. The mathematics used is of the simplest possible nature.

There are a few mistakes. On page 110, line 9, we find "solute" for "solution," and at the bottom of page 223 "cath-

ode" and "anode" should be transposed. The use of Q for different quantities on pages 135 and 315 might confuse the beginner. On page 227 we read the astonishing statement that, "if in an hour a gram equivalent of sodium and of chlorine are discharged at the respective electrodes, the current which has passed through the cell is $2 \times 96540 \div 3600 = 53.6$ amperes," *i. e.*, a faraday for each ion.

The moderate price is an attractive feature in view of the heavy outlay of the scientific student for books, and the frequency of new editions to keep pace with rapid advance of this branch of science. In the opinion of the reviewer, the book is one of the best elementary texts that have appeared, and deserves a cordial welcome. JOEL H. HILDEBRAND.

LES BASES PHYSICO-CHIMIQUES DE LA CHIMIE ANALYTIQUE. PAR LE DR. W. HERZ, Professeur à l' Université de Breslau. Traduit de l' allemand par E. PHILIPPI, Licencié ès Sciences. Paris: Gauthier-Villars. 1909. pp. 167.

The scope of this little book can be seen best from its contents. The twelve chapters and an introduction deal with: The Gas Laws, Theory of Solutions, Abnormal Molecular Weights, Theory of Electrolytic Dissociation, Law of Electroneutrality of Solutions, Ionization and Physical Properties, Colloidal Solutions, Solid Solutions, Chemical Mechanics, Law of Mass Action and Electrolytic Dissociation, Heterogeneous Systems, The Different Phases in a Heterogeneous System, and Velocity of Reaction in a Homogeneous System.

The book is clearly written and will doubtless prove to be useful in the field which it is meant to cover. H. C. J.

A MANUAL OF VOLUMETRIC ANALYSIS FOR THE USE OF PHARMACISTS, SANITARY AND FOOD CHEMISTS, AS WELL AS FOR STUDENTS IN THESE BRANCHES. BY HENRY W. SCHIMPF, PH.G., M.D., Professor of Analytical Chemistry, Brooklyn College of Pharmacy, etc., etc. Fifth Edition, Revised and Enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xx + 725, 102 Figures. Price, $5.

The earlier editions of this text-book are well-known to many analysts, especially to pharmacists, for whom they have been mainly prepared. The present edition is the result of an extensive revision and enlargement, to give it the character of a "Manual" of volumetric analysis. Part I opens with a series of chapters on such general topics as indicators (an exhaustive discussion), apparatus, and methods of calculation, and are followed by chapters on neutralization methods, precipitation methods, and oxidation and reduction processes. Part II includes chapters on the volumetric methods for the

determinations of the common organic and inorganic acid radicals and of each of the more common metals. Part III treats of sanitary analyses and the volumetric analysis of organic medicinal substances. Part IV deals with a few gasometric methods, and the book closes with a most complete index, covering more than twenty-six pages.

Like the former editions, the manual in its present form is prepared with the needs of the pharmacist chiefly in mind and no pains are spared to make many points clear to those analysts, who, as a rule, are not able to spend any considerable amount of time in the preliminary study of chemistry as such. This is particularly true with reference to equations and the calculation of results of analysis and there is an almost unnecessary repetition of simple directions and statements throughout the book. A considerable variety of procedures are outlined for nearly every determination, but it is at least open to question whether a smaller number more fully and occasionally more accurately described would not have been more valuable as a guide. In some instances, as for example the standardization of a solution of sulphuric acid by precipitation of barium sulphate on page 73, the directions given are wholly inadequate to secure accurate results. As a whole, however, the book in its present form is likely to prove useful. It is well printed, and well provided with references to original articles bearing upon the procedures cited.   H. P. TALBOT.

LABORATORY METHODS OF INORGANIC CHEMISTRY. BY HEINRICH BILTZ, University Kiel, and WILHELM BILTZ, University Göttingen. Authorized translation by WILLIAM T. HALL and ARTHUR A. BLANCHARD, Massachusetts Institute of Technology New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xv + 246. Price, $3.

This volume is the largest and best book on inorganic preparations yet published. It is not a mere collection of recipes like many manuals. The one hundred and sixty-one preparations are used as illustrations of some law or special method; for example, the chapter on elements includes reduction processes by carbon, by aluminothermy, by potassium cyanide and by aqueous reducing agents, desulphurization of sulphides by the precipitation and roasting processes, cupellation and preparation of metals by electrolysis, each with illustrative preparations. Under allotropy the allotropic silver sulphide and sulphur and the transformation points of cuprous and silver mercuro-iodides are shown. The passive state is studied in passive iron, the amorphous condition in amorphous sulphur, the colloidal state and adsorption compounds in colloidal

platinum, colloidal antimony sulphide, lanthanum blue, molybdenum blue, and colloidal gold solutions. The theories of Werner are illustrated by a large number of metal-ammonia compounds. The book closes with a valuable chapter on methods of preparing the rare elements, including radium, from their ores. These few references will suffice to show the nature and scope of the book which is written from the modern physical-chemical standpoint; indeed, much of the volume might be called physical chemistry, theoretical and applied.

It is scarcely necessary to say that this is not a book for the average undergraduate; students who have some knowledge of chemistry and familiarity with laboratory work will find its study fascinating and stimulating.   E. R.

PRACTICAL TESTING OF GAS METERS. By C. H. STONE, B.S., M.S., Chief Inspector of Gas, Public Service Commission, Second District, New York. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. x + 337, 51 Figures. Price, $3.50.

Under this modest title the author presents a handsome volume of 336 pages in which he gives a thorough and most interesting account of photometry, chemical tests, calorimetry, specific gravity, pressure and testing of meters.

To quote the preface, "so far as the writer knows, no book, written by an American and dealing purely with American method of gas manufacture and testing and thoroughly up-to-date, is available to-day." . . . "The writer's chief aim has been to explain clearly, simply and fully such tests as would be of practical service to the gas manufacturer, chemist or photometrist and to make such comments as might guide him in his choice of apparatus or process." . . . Mr. Stone knows his subject thoroughly; he describes in detail the newest methods and the newest improved forms of apparatus.   E. R.

AMERICAN

CHEMICAL JOURNAL

THE CONDUCTIVITIES, DISSOCIATIONS, AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY BETWEEN 35° AND 80° OF SOLUTIONS OF A NUMBER OF SALTS AND ORGANIC ACIDS.

By A. M. Clover and Harry C. Jones.

A large amount of work has been done on the conductivity of solutions of electrolytes at different temperatures. If, however, we consult any compilation of data on this subject, or all of the compilations together, we shall be impressed by the fact that the work in this field has not been systematic, and that the very facts that we most desire are often not available. Again, the range over which conductivity measurements have, for the most part, been made is from 0° to 25°, and frequently the conductivities of a substance have been measured only at one temperature. This often applies to very important compounds.

We measure dissociation usually by the conductivity method, and since chemical activity is so directly connected with dissociation, it is obviously very important that we should know the dissociation of any electrolyte at the temperature

at which it is entering into a chemical reaction. For small ranges in temperature, the dissociation of an electrolyte does not change very greatly, but for even small changes in temperature, the velocity of the ions undergoes very marked change, and the more rapidly the ions move, other things being equal, the greater their chemical activity.

It was with the object of supplying the very important data relative to conductivity at different temperatures, that work was undertaken on this problem in this laboratory nine years ago. Jones and Douglas[1] in 1901 published their paper on "The Association of Certain Acids, Bases and Salts at Different Temperatures." In this work the conductivities of hydrochloric acid, nitric acid, sulphuric acid, potassium hydroxide, sodium hydroxide, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, sodium nitrate, ammonium nitrate, potassium sulphate, and potassium permanganate, at dilutions ranging from normal to several thousandths normal, were measured, and from these results the dissociations at the various temperatures calculated. The conductivities were measured at 0° as the lowest temperature, and 35° as the highest, also at 25° and at the temperature of hydrant water, which was usually around 10° to 15°. From this earlier work the conclusion was drawn that the temperature coefficient of conductivity increases with the dilution of the solution. For salts, the temperature coefficient increases with rise in temperature, but for acids and bases there is very little change in the coefficient with temperature.

It was shown in this earlier work that for the range of temperature studied, the dissociation did not change to any great extent. It was pointed out that this is in accord with the approximate agreement between the dissociation as measured by the freezing point method by Jones[2] and the dissociation as determined by the Kohlrausch conductivity method. The former results were obtained at temperatures slightly below 0°, while the latter were obtained at 18°.

[1] This Journal, **26**, 428 (1901).
[2] Z. physik. Chem., **11**, 110, 529; **12**, 623 (1893).

The method of making the conductivity measurements was greatly improved after this earlier work was done. A large number of details were worked out, and some sources of error in the earlier work eliminated or reduced to a minimum. The next work on this problem was undertaken in 1904 and published in 1905[1] by Jones and West. This investigation extended over the same range of temperature as that of Jones and Douglas, *viz.*, from 0° to 35°. They worked with solutions of ammonium chloride, ammonium bromide, sodium bromide, sodium iodide, sodium carbonate, sodium acetate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, potassium sulphate, potassium bisulphate, potassium carbonate, potassium ferrocyanide, calcium chloride, calcium bromide, strontium bromide, barium chloride, magnesium chloride, zinc sulphate, manganese chloride, manganese nitrate, cobalt chloride, cobalt nitrate, nickel chloride, nickel nitrate, copper chloride, copper nitrate, hydrochloric acid, nitric acid, sulphuric acid, and oxalic acid. The concentrations used ranged from a volume of two to that of over eight thousand. The temperatures were 0°, that of the hydrant water, 25° and 35°. A number of improvements in the method as earlier used were made and the results obtained are more accurate than those in the earlier work. It was found that over the range in temperature between 0° and 35° the dissociation decreased with rise in temperature. This is in accord with the investigations of Noyes[2] and coworkers at higher temperatures. It was also shown that the percentage temperature coefficients of conductivity decrease with rise in temperature from 0° to 35°.

It was pointed out that these facts are of interest in connection with certain theories that have been proposed, connecting the dissociating power and certain other physical properties of solvents. Thus, Dutoit and Aston[3] showed that the more associated a solvent the greater its dissociating power, and while this relation is not quantitative, there is undoubtedly a large element of truth in it. With rise in tem-

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[1] This Journal, **34**, 357 (1905).
[2] Monograph No. 63, Carnegie Institution of Washington.
[3] Compt. Rend., **125**, 540 (1897).

perature the association of liquids becomes less and less and their dissociating power becomes smaller.

The results obtained are also in accord with the Thomson[1]–Nernst[2] hypothesis, connecting the dielectric constants of solvents with their dissociating power. The dielectric constants of solvents decrease with rise in temperature, and the dissociating power of solvents decreases with rise in temperature. Theory and fact are thus in perfect accord.

The next investigation was on the conductivity and ionization of electrolytes in aqueous solutions as conditioned by temperature, dilution and hydrolysis, by Jones and Jacobson.[3] The methods earlier used were still further improved, and the following compounds studied: Lithium chloride, lithium bromide, lithium nitrate, lithium sulphate, sodium nitrate, disodium phosphate, potassium sulphocyanate, potassium chromate, potassium dichromate, calcium nitrate, strontium chloride, strontium nitrate, strontium formate, barium bromide, barium nitrate, barium formate, barium acetate, magnesium sulphate, cupric bromide, chromium chloride, chromium nitrate, ferric chloride, ferric nitrate, nickel sulphate, nickel acetate, cobalt sulphate, cobalt acetate, lead nitrate, trichloracetic acid, racemic acid, picric acid, propionic acid, o-nitrobenzoic acid, and m-nitrobenzoic acid.

The range of dilution was usually from volume 2 to volume 2048. Occasionally higher dilutions were employed. The range of temperature was from 0° to 35°, the conductivities being measured also at 25°, and at a temperature that was not far from 10°. Results of the same general character were obtained as in the earlier investigations. It was shown that conductivity is not a linear function of the temperature at any dilution worked with, the increase in conductivity with rise in temperature being greater the higher the temperature. The conductivities are parabolic functions of the temperature. The importance of hydrolysis as affecting conductivity is also pointed out. The temperature coefficients of conductivity of a number of organic acids have been

[1] Phil. Mag., **36**, 320 (1894).
[2] Z. physik. Chem., **13**, 531 (1894).
[3] THIS JOURNAL, **40**, 355 (1908).

measured in this laboratory by Mr. G. F. White, and some of the results have been published in THIS JOURNAL.[1]

A number of relations between the temperature coefficients of conductivity and the present hydrate theory were pointed out by Jones.[2] Since most of the ions are hydrated and since the complexity of the hydrate decreases with rise in temperature, the mass of the ion would decrease with rise in temperature. Therefore, if everything else remained unchanged the conductivity would increase from this cause alone. We should, then, expect to find that *those ions which have the largest hydrating power would have the largest temperature coefficients of conductivity.* That such is the case has already been shown to be the fact.[3]

Since the complexity of the hydrate is greater the higher the dilution, we should expect a greater change in the complexity of the hydrate with change in temperature at higher than at lower dilutions. In a word, *the temperature coefficient of conductivity for any given substance is greater at a high than at a low dilution.* This conclusion is also established by the facts.[4]

The large change in conductivity with rise in temperature is due, then, in part to *the decreasing complexity of the hydrates formed around the ions.* If other things remained equal, this would cause the ions to move faster through the solvent.

It is, of course, at the same time true that, with rise in temperature, the solvent is becoming less viscous, and this also would increase the velocity of the ions.

The object of the present investigation is to extend the earlier work from 35° to as high temperature as can be employed with solutions in ground-glass stoppered vessels. We find that we can work very satisfactorily up to 65° when we take sufficient precautions. The more concentrated solutions can be studied even up to 80°.

It seems to us to be a matter of very considerable importance for chemistry to know the conductivity of solutions over the

[1] **42**, 520 (1909).
[2] THIS JOURNAL, **34**, 357 (1905).
[3] *Ibid.*, **35**, 448 (1906); **40**, 404 (1908).
[4] *Ibid.*, **35**, 449 (1906).

range in temperature indicated above, since so many chemical reactions take place and so much chemical work is done within these temperature limits. Further, when we examine the literature we find that comparatively few reliable conductivity measurements have been made over this temperature range, and where such measurements have been made the temperatures chosen have been so far apart that we cannot calculate the temperature coefficients for any narrow range in temperature with any high degree of accuracy.

It is with the idea of supplying these data that the present work was done, and we intend to include within its scope practically all of the more important inorganic and organic compounds.

EXPERIMENTAL PART.

Apparatus.

The cells used were of the same general type as those employed in previous investigations on a similar problem in this laboratory and described by Jones and Lindsay[1] and Jones and West[2]. The ground-glass stoppers of the cells were hollow, the upper and lower surfaces being about 3 cm. apart. The hollow glass tubes carrying the electrodes were sealed directly into the stoppers, since the use of sealing wax, which had been previously employed for holding the electrode tubes in place, was inadmissible at the temperatures to which the cells were subjected in this work. The electrodes were coated with platinum black and then heated in the blast lamp. Seven or eight cells were used, each cell being employed regularly for a certain strength of solution. The distance separating the electrodes varied from about 4.5 cm. in the case of the cell used in measuring the most concentrated solutions to about 3.5 mm. in the case of the cell used for the most dilute solutions.

The Kohlrausch method involving the use of an ordinary Wheatstone bridge was employed. The bridge wire, resistance box and the thermometers used in regulating the temperatures of the baths were all calibrated in the same way

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[1] THIS JOURNAL, **28**, 329 (1902).
[2] *Ibid.*, **34**, 336 (1905).

as that described by previous workers in this laboratory.

Measurements were made at four different temperatures, namely, 35°, 50°, 65° and 80°. For thermostats, two galvanized tubs were used, each having a capacity of 25 or 30 liters. These were heated with a gas flame regulated by hand and the water was stirred by means of a motor. The bath used for measurements at 35° and 50° was protected on the sides by a sheet of thick asbestos. The other bath, which was used in working at 65° and 80°, was in addition protected on the bottom by a sheet of thick asbestos, in which a small hole was made for heating. The sides of this vessel were double walled, the intermediate space being packed with finely divided asbestos and magnesia. It was an easy matter to maintain a constant temperature in these baths to within 0°.05 during the time required to bring the cell contents to temperature equilibrium and make the necessary readings.

It was possible to immerse the cells in the bath almost completely, but as the cells were nearly filled with the solution, it was desirable to maintain the air above the water of the bath at a temperature as near that of the bath as practicable. With the bath at 35° this difference in temperature is inconsiderable, but for higher temperatures, two rectangular pieces of glass were used for a covering, each being placed over one-half of the bath. The stirrer and the thermometer passed between these two plates. A number of circular holes were cut in the glass plates at the proper places so that the copper wires used in making connection with the cells could be introduced from the outside without any trouble. The mercury cups used in connecting these wires were movable and were placed on top of the glass cover. The plates were elevated slightly at the edges of the bath so that the water which condensed upon the plates ran toward the middle and dropped back into the bath. This arrangement was found to be very convenient and entirely satisfactory. At 80° the temperature of the air space above the water was only about 15° lower than that of the bath and at the other temperatures the difference was considerably less.

Preparation of Solutions.

The chemicals used were all obtained from the firm of
C. A. F. Kahlbaum. In every case the purest obtainable
substance was used and this was further purified by several
recrystallizations. Where other methods of purification or
preparation were employed they will be described in detail
under the heading of the given substance. Unless other-
wise specified the salts used were first dried in a desiccator
after recrystallization, then pulverized and dried to constant
weight in an air bath at 170°. The ammonium salts were
treated in the same manner, but were dried at 100°. All
purified substances were preserved until used in glass-stop-
pered bottles placed in a desiccator. Wherever possible
the 0.5 gram-molecular solution, which was the highest con-
centration used, was made by directly weighing the sub-
stance. Where this was not possible the substance was dis-
solved in water and its concentration determined by analysis;
from this stock solution the required amount (from 75 cc.
to 100 cc.) was measured by means of a calibrated 100 cc.
burette.

Since the coefficient of expansion of water increases greatly
with the temperature, it was necessary to take care in regard
to having the solutions made at the *exact temperature* at which
they were to be measured or to applying the proper correc-
tion. The solutions measured at 50°, 65° and 80° were pre-
pared at these temperatures, respectively. The solutions
prepared at 50° were also used for the measurements at 35°,
and the correction factor 0.994 was then applied to all dilu-
tions except the 0.5 gram-molecular solutions, for which the
factor 0.993 was used.[1]

From the solution of greatest concentration all the others
were prepared by dilution, by means of pipettes and measur-
ing flasks. All of the measuring vessels employed were care-
fully calibrated by means of pure water, and the weights re-
duced to a vacuum. The water used for the solutions was
prepared in the manner described by previous workers in
this laboratory, and it had a conductivity varying from 1.5

[1] Landolt–Börnstein: Physikalisch-chemische Tabellen, Berlin, 1905.

to 2.0×10^{-6}. The correction which must be applied for the conductivity of the water is of course much larger at higher temperatures, and was carefully determined in duplicate, in two cells, just before the measurement of the solutions.

Cell Constants.

The greatest obstacle which has been encountered in this work relates to the constants of the cells.

It has developed that a strain is brought about by the high temperatures which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates. Naturally, these changes are manifested chiefly in those cells in which the electrodes are relatively close together. The electrodes have been removed and again sealed into the glass, and have also been again ignited in the blast lamp, but the same behavior has persisted.

Since such a variation had not previously been observed in work covering a range from 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°. Although this procedure was continued for several months, it was found that the changes were not entirely prevented, although they were not as frequent as they had previously been. It was due largely to this cause that no measurements of the more dilute solutions at 80° were attempted in these cells.

The changes in the value of the cell constant just considered sometimes amounted to one per cent. The constants were measured at least once a week throughout the course of this work, and it is by this means that it has been possible to secure fairly accurate results in the case of the dilute solutions, since all variations have been quickly noted and by taking a mean of the two values the error has been reduced to a minimum.

Some other interesting results have been obtained which

bear upon the strict reliability of the cell constants when used at elevated temperatures with dilute solutions. A series of measurements was arranged which should serve as a check upon the accuracy of the entire procedure followed regularly in obtaining the results described and recorded in this paper. There are several possible sources of error, such as the solubility of the glass and the effect of the solute upon the glass, the evaporation of the solvent, the presence of air bubbles, and other errors due to difficulties in manipulation at an elevated temperature. Most of the possible sources of error concern only the dilute solutions. Accordingly several different substances were measured at 3 dilutions (5, 1024 and 2048) in the cells ordinarily used for solutions of this strength. The measurements were first carefully made at 35° and duplicated, then the regular systematic procedure was gone through at 65°, and after this readings at 35° were again made. If the results obtained the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found that in over one-half the cases at 80° the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours) *the reading slowly changed back in all cases to the original value.* Although these changes amount to less than 3 mm. on the bridge this was sufficient to cause the difference referred to, and is greater than any possible error in the reading. It is difficult to see what other cause can be assigned to these results than a temporary change in the cell constant during the heating at 65°.

In determining the cell constants, a 0.02 N solution of potassium chloride was employed for those cells used in measuring the stronger solutions and a 0.002 N normal solution of the same substance for the remaining cells. The value 129.7 for μ_v 25° for the 0.02 N potassium chloride solution was used, and from this the mean value 137.5 was found, as the result of several experiments, for μ_v 25° for the 0.002 N solu-

tion. This is in good agreement with 137.7, the value obtained by Jacobson.[1]

Solubility of Glass.

In conductivity work at ordinary temperatures this factor has always been neglected, and probably is not sufficiently large to influence the results even with very dilute solutions. However, at 50° the error introduced by this factor at a dilution of 1000 is greater than any of the other ordinary experimental errors. At 65° the solubility of the glass is still greater, and at 80° the conductivity of pure water is increased tenfold on remaining in the cell for a couple of hours. In this connection it may be stated that the cells employed were made of hard glass. Of course, the amount of glass dissolved depends upon the exact nature of the latter and was found to vary considerably with the different cells used, and at different intervals in the case of any one cell. The idea of introducing a correction for the solubility of the glass was abandoned but the difficulty was overcome in another way. It was found that after the cells had been heated with water for several days the amount of glass dissolved gradually decreased and finally amounted to practically nothing. After this treatment, as the cells were kept in a bath at 45° to 50° and the water in them changed once a day, the solubility of the glass at 65° was always practically nothing, or entirely negligible. If a cell were removed from the bath and allowed to stand filled with water at the room temperature for any length of time, it was found that glass was again dissolved on heating, It is quite certain that this factor does not stand in the way of very accurate work at 65°, but at 80° the question was not studied on account of the changes in the cell constants, which has already been discussed.

Procedure.

A number of difficulties in manipulation were encountered at the beginning, and it was only after some experience and practice that it was possible to do careful work with the desirable rapidity.

[1] This Journal, **40**, 364 (1908).

At a temperature of 25° or lower the formation of air bub-
bles upon the plates is so slight that they may be entirely
neglected. At 35° there is a noticeable formation of bubbles
during the 20 or 30 minutes required for complete temperature
equilibrium. At 50° and 65° the bubbles are much more
abundant. If, however, at these latter temperatures, the
cells are allowed to remain in the bath for nearly an hour,
the formation of bubbles ceases, and if the bubbles are re-
moved by taking out the cell and agitating the solution, no
more appear. For this reason, it was necessary in working
at 50° and 65° to allow all solutions to remain in the bath
for an hour before proceeding farther. At 80° the formation
of bubbles ceases in much less time.

For several reasons the cells were nearly filled with the
solution: First, to minimize any slight change in concentra-
tion brought about by condensation or escape of the solvent,
or from any other cause. Second, to exclude the air with
its accompanying carbon dioxide from the cell, as the dioxide
would be dissolved during the manipulation and would in-
fluence the results with dilute solutions. Third, to prevent
difficulty in opening the cells. With a large air space dimin-
ished pressure is quickly produced on removal from the bath,
and if the cells can be opened at all it can be done only at the
risk of distorting the electrodes.

After the formation of bubbles had ceased and the solu-
tions had been gently agitated to clear the plates, the cells
were replaced in the bath and readings made as soon as tem-
perature equilibrium had been reached. The entire procedure,
including the removal of the cell and agitation of the solution,
was then repeated as a check upon the first.

After the measurements at 50° had been completed the
bath was cooled to 35°, and without changing the solution
measurements were made and duplicated at the latter tem-
perature. In this way it was possible to use one set of solu-
tions for both temperatures, and the difficulty with air bub-
bles encountered on measuring directly at 35° was entirely
avoided. It was necessary to heat the cells again to 50°
or above in order to open them. When not in use the cells

which were not kept in the bath at 45° to 50° were filled with pure water.

<div align="center">

Units.

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In conformity with previous work of this nature published from this laboratory the conductivity values are expressed in Siemens units, and the molecular conductivities in all cases refer to gram molecules of the substances.

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Lithium Chloride.

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The salt was recrystallized once and was then dissolved in water. The lithium in this solution was determined as the sulphate and the 0.5 gram-molecular solution was prepared from it by volume.

Table I.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	92.34	69.9	117.7	69.4	144.1	68.4
8	107.2	81.1	136.7	80.6	167.7	79.6
32	116.7	88.3	149.8	88.4	185.6	88.1
128	124.1	93.9	159.3	94.0	199.0	94.5
512	128.6	97.3	165.2	97.5	205.3	97.5
1024	130.2	98.6	167.5	98.8	208.3	98.9
2048	132.1	100.0	169.5	100.0	210.6	100.0

Table II.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.69	1.83	1.76	1.50
8	1.97	1.84	2.07	1.51
32	2.21	1.89	2.39	1.60
128	2.35	1.89	2.65	1.66
512	2.44	1.90	2.67	1.62
1024	2.49	1.91	2.72	1.62
2048	2.49	1.88	2.74	1.62

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Sodium Chloride.

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The salt was purified by precipitation from solution with hydrochloric acid gas, recrystallization from dilute hydrochloric acid, and a final recrystallization from pure water.

Table III.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v 80°.
2	104.6	72.4	132.6	71.8	161.8	70.8	191.8
8	118.3	81.9	150.5	81.5	184.5	80.7	220.1
32	129.0	89.3	164.3	89.0	201.0	88.0	242.0
128	137.2	95.0	175.4	95.0	214.7	94.0	256.2
512	141.6	98.1	181.1	98.0	222.9	97.5	...
1024	143.4	99.3	183.2	99.2	225.5	98.7	...
2048	144.4	100.0	184.7	100.0	228.5	100.0	...

Table IV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.87	1.79	1.95	1.47	2.00	1.24
8	2.15	1.82	2.27	1.51	2.37	1.28
32	2.35	1.82	2.45	1.49	2.73	1.36
128	2.55	1.86	2.62	1.49	2.77	1.29
512	2.63	1.86	2.79	1.54	..	..
1024	2.65	1.85	2.82	1.54	..	..
2048	2.69	1.86	2.92	1.58	..	..

Sodium Bromide.

Table V.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v 80°.
2	106.25	74.7	131.1	72.0	162.6	71.6	196.2
8	119.2	83.8	151.4	83.2	184.1	81.1	222.6
32	129.1	90.7	164.5	90.4	201.0	88.5	243.7
128	136.7	96.1	174.6	95.9	212.6	93.7	259.6
512	140.5	98.7	180.1	98.9	219.5	96.7	...
1024	141.4	99.4	180.9	99.4	222.8	98.2	...
2048	142.3	100.0	182.0	100.0	227.0	100.0	...

Table VI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.66	1.56	2.10	1.60	2.24	1.38
8	2.15	1.80	2.18	1.44	2.57	1.40
32	2.36	1.83	2.43	1.48	2.85	1.42
128	2.53	1.85	2.53	1.45	3.13	1.47
512	2.64	1.88	2.63	1.46	..	..
1024	2.63	1.86	2.79	1.54	..	..
2048	2.65	1.86	3.00	1.65	..	..

Sodium Nitrate.

Table VII.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		
	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	95.05	69.2	120.1	68.5	146.0	68.5	173.5
8	111.3	81.1	141.1	80.5	171.4	80.4	203.6
32	122.8	89.4	155.7	88.9	189.0	88.6	225.4
128	129.6	94.4	164.8	94.1	201.3	94.4	241.8
512	134.4	97.9	171.0	97.6	209.6	98.3	...
1024	135.8	98.9	173.1	98.8	213.2	100.0	...
2048	137.3	100.0	175.2	100.0	213.2	100.0	...

Table VIII.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.67	1.76	1.73	1.44	1.83	1.25
8	1.99	1.79	2.02	1.43	2.15	1.25
32	2.19	1.78	2.22	1.43	2.43	1.29
128	2.35	1.81	2.43	1.47	2.70	1.34
512	2.44	1.82	2.57	1.50	..	..
1024	2.49	1.83	2.67	1.54	..	..
2048	2.53	1.84	2.53	1.44	..	..

Sodium Sulphate.

The purified salt was pulverized and dried to constant weight at 150°.

Table IX.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		
	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	134.5	46.1	172.5	45.9	205.4	43.8	248.1
8	173.7	59.5	221.8	59.0	274.3	58.5	331.9
32	204.6	70.1	262.2	69.7	337.2	71.9	410.7
128	233.1	79.9	320.4	85.2	399.0	85.1	474.3
512	273.6	93.8	353.2	93.9	437.9	93.4	...
2048	288.0	98.7	372.6	99.1	462.5	98.7	...
4096	291.8	100.0	376.0	100.0	468.7	100.0	...

Table X.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.53	1.88	2.19	1.27	2.85	1.39
8	3.21	1.85	3.50	1.58	3.84	1.40
32	3.84	1.88	5.00	1.91	4.90	1.45
128	5.82	2.50	5.24	1.64	5.02	1.26
512	5.31	1.94	5.65	1.60	..	..
2048	5.64	1.96	5.99	1.61	..	..
4096	5.61	1.92	6.18	1.64	..	..

Potassium Chloride.

Table XI.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		
	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	129.6	77.4	161.9	76.3	193.7	76.4	226.5
8	142.5	85.1	179.1	84.4	215.9	83.3	254.4
32	152.8	91.2	192.8	90.9	234.1	90.3	277.4
128	161.9	96.7	204.3	96.3	247.1	95.3	292.8
512	165.6	98.9	209.1	98.6	255.8	98.6	...
1024	167.7	100.1	211.6	99.8	258.3	99.6	...
2048	167.5	100.0	212.1	100.0	259.3	100.0	...

Table XII.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.15	1.66	2.12	1.31	2.19	1.13
8	2.44	1.71	2.45	1.37	2.57	1.19
32	2.67	1.75	2.75	1.43	2.89	1.23
128	2.83	1.75	2.85	1.40	3.05	1.23
512	2.90	1.75	3.11	1.49	..	..
1024	2.93	1.75	3.11	1.47	..	..
2048	2.97	1.77	3.15	1.49	..	..

Potassium Bromide.

Table XIII.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		
	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	133.2	77.7	165.1	76.2	196.7	74.6	231.6
8	145.4	84.8	181.4	83.7	218.1	82.7	257.8
32	155.6	90.8	195.3	90.1	236.5	89.7	280.9
128	164.2	95.8	206.0	95.1	250.0	94.8	300.0
512	167.7	97.8	211.6	97.6	256.6	97.3	...
1024	169.0	98.6	213.6	98.6	260.3	98.7	...
2048	171.4	100.0	216.7	100.0	263.7	100.0	...

Table XIV.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.13	1.60	2.11	1.28	2.33	1.18
8	2.40	1.65	2.45	1.35	2.65	1.22
32	2.65	1.70	2.75	1.41	2.96	1.25
128	2.79	1.70	2.93	1.42	3.33	1.33
512	2.93	1.75	3.00	1.42	..	..
1024	2.97	1.76	3.11	1.46	..	..
2048	3.02	1.76	3.13	1.45	..	..

Potassium Nitrate.

Table XV.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		$\mu_v 80°.$
	$\mu_v.$	$\alpha.$	$\mu_v.$	$\alpha.$	$\mu_v.$	$\alpha.$	
2	113.2	70.4	141.3	69.8	170.0	69.0	205.1
8	131.8	81.9	165.0	81.5	199.6	81.0	236.9
32	145.3	90.3	182.0	89.9	220.4	89.4	260.2
128	154.7	96.1	194.1	95.9	235.4	95.5	278.6
512	159.1	98.9	199.8	98.7	242.1	98.3	...
1024	161.2	100.2	202.7	100.1	245.2	99.5	...
2048	160.9	100.0	202.5	100.0	246.1	100.0	...

Table XVI.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.87	1.65	1.91	1.35	2.34	1.38
8	2.21	1.68	2.31	1.40	2.49	1.25
32	2.45	1.69	2.56	1.41	2.65	1.20
128	2.63	1.70	2.75	1.42	2.88	1.22
512	2.71	1.70	2.82	1.41	..	..
1024	2.77	1.72	2.83	1.40	..	..
2048	2.77	1.72	2.91	1.44	..	..

Potassium Sulphate.

Table XVII.—Molecular Conductivity.

V.	$\mu_v 35°.$	$\mu_v 50°.$	$\mu_v 65°.$	$\mu_v 80°.$
2	181.1	224.8	267.2	307.7
8	220.3	276.7	332.8	390.8
32	259.7	329.2	400.0	473.1
128	296.9	376.0	456.2	547.7
512	319.6	406.7	500.7	...
1024	328.2	419.6	513.1	...

Table XVIII.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.91	1.61	2.83	1.26	2.70	1.01
8	3.76	1.71	3.74	1.35	3.87	1.16
32	4.63	1.78	4.72	1.43	4.87	1.22
128	5.27	1.77	5.35	1.42	6.10	1.34
512	5.81	1.82	6.27	1.54	..	..
1024	6.09	1.86	6.23	1.48	..	..

Potassium Chromate.

Table XIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	200.5	249.1	295.9
8	237.3	297.5	357.7
32	272.7	343.8	417.4
128	307.9	389.4	468.5
512	326.7	415.0	513.6

Table XX.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.24	1.62	3.12	1.25
8	4.01	1.69	4.01	1.35
32	4.74	1.74	4.91	1.43
128	5.43	1.76	5.27	1.35
512	5.89	1.80	6.57	1.58

Potassium Acetate.

The salt was prepared by neutralizing a quantity of acetic acid with the best quality of potassium hydroxide from alcohol, evaporating to dryness and then dissolving the product in water and neutralizing with a small additional amount of acetic acid. The acetic acid used was recrystallized twice by cooling, and was then dissolved in water and the strength of the solution determined as in the case of oxalic acid (see p. 210). The exact amount of acetic acid used in preparing the salt was accordingly known and the solution of the salt was brought to a definite volume and used in preparing the solution for measurement.

Table XXI—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	101.7	77.9	129.2	77.5	157.4	74.7
16	113.7	87.1	144.6	86.7	177.1	84.0
64	121.7	93.3	155.0	93.0	190.4	90.3
256	127.0	97.3	162.3	97.4	199.7	94.7
1024	129.4	99.2	165.1	99.0	203.7	96.6
2048	130.5	100.0	166.7	100.0	210.8	100.0

Table XXII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.83	1.80	1.88	1.46
16	2.06	1.81	2.17	1.50
64	2.22	1.82	2.36	1.52
256	2.35	1.85	2.49	1.53
1024	2.38	1.84	2.57	1.56
2048	2.41	1.85	2.94	1.76

Potassium Benzoate.

The salt was prepared from a weighed quantity of pure benzoic acid in exactly the same way as potassium acetate. The benzoic acid was purified by recrystallizing several times from water, pulverizing and drying *in vacuo*.

Table XXIII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		
V.	μ_v.	α.	μ_v.	α.	μ_v65°.
16	102.5	85.9	131.1	86.1	160.4
32	107.5	90.1	137.0	90.0	167.3
64	110.9	93.0	141.6	93.0	173.2
128	114.7	96.1	146.7	96.3	...
512	118.6	99.4	151.1	99.2	...
1024	119.3	100.0	152.3	100.0	...

Table XXIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	1.91	1.86	1.95	1.49
32	1.97	1.83	2.02	1.47
64	2.05	1.85	2.11	1.49
128	2.13	1.86	..	...
512	2.17	1.83	..	...
1024	2.20	1.84	..	...

Ammonium Chloride.

Table XXV.—Molecular Conductivity and Percentage Dissociation.

V.	35°.		50°.		65°.		
	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	129.2	75.2	161.4	73.9	194.0	73.1	227.7
8	142.3	82.8	179.4	82.2	217.1	81.8	256.5
32	153.2	89.1	194.0	88.9	235.9	88.9	279.3
128	162.8	94.7	206.2	94.4	251.1	94.6	296.4
512	166.8	97.0	211.4	96.8	259.5	97.8	...
1024	169.0	98.3	214.4	98.2	269.7	101.6	...
2048	171.9	100.0	218.3	100.0	265.4	100.0	...

Table XXVI.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.		65° to 80°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.15	1.66	2.17	1.34	2.25	1.16
8	2.47	1.74	2.51	1.40	2.63	1.21
32	2.72	1.78	2.79	1.44	2.89	1.23
128	2.89	1.78	2.99	1.45	3.02	1.20
512	2.97	1.78	3.21	1.52	..	..
1024	3.03	1.79	3.69	1.72	..	..
2048	3.09	1.80	3.14	1.44	..	..

Ammonium Nitrate.

Table XXVII.—Molecular Conductivity and Percentage Dissociation.

V	35°.		50°.		65°.	
	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	119.5	73.2	148.9	72.5	179.8	71.5
8	135.2	82.8	169.3	82.5	204.3	81.2
32	146.4	89.7	184.2	89.7	223.0	88.6
128	154.9	94.9	195.2	95.1	237.5	94.4
512	158.9	97.4	201.4	98.1	246.3	97.9
1024	160.2	98.2	203.7	99.2	249.3	99.1
2048	163.2	100.0	205.3	100.0	251.6	100.0

Table XXVIII.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.96	1.64	2.06	1.38
8	2.27	1.68	2.33	1.38
32	2.52	1.72	2.59	1.41
128	2.69	1.74	2.82	1.44
512	2.83	1.78	2.99	1.48
1024	2.90	1.81	3.04	1.49
2048	2.81	1.72	3.09	1.51

Ammonium Sulphate.

Table XXIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°	μ_v 80°.
2	172.8	215.8	257.6	300.1
8	215.1	270.8	325.2	381.1
32	256.3	324.3	393.3	465.2
128	295.7	375.8	461.7	537.1
512	326.3	417.0	506.5	...
2048	335.0	428.4	528.2	...
4096	344.1	440.0	538.6	...

Table XXX.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.87	1.66	2.79	1.29	2.83	1.10
8	3.71	1.72	3.63	1.34	3.73	1.15
32	4.53	1.77	4.60	1.42	4.79	1.22
128	5.34	1.81	5.73	1.52	5.03	1.09
512	6.05	1.85	5.97	1.43	..	..
2048	6.23	1.86	6.65	1.55	..	..
4096	6.39	1.86	6.57	1.49	..	..

Barium Chloride.

The recrystallized salt was dried in a desiccator, then pulverized and dried to constant weight in an air bath at 150°.

Table XXXI.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.	μ_v 80°.
2	176.4	220.6	259.8	310.2
8	216.0	272.4	322.3	387.3
32	247.6	313.9	375.3	455.1
128	274.2	348.7	421.5	509.2
512	295.7	378.0	453.8	...
2048	308.4	395.0	478.0	...

Table XXXII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.95	1.67	2.61	1.18	3.36	1.29
8	3.76	1.74	3.33	1.22	4.33	1.34
32	4.42	1.79	4.09	1.30	5.32	1.42
128	4.97	1.81	4.85	1.39	5.85	1.39
512	5.49	1.86	5.05	1.34	..	..
2048	5.77	1.87	5.53	1.40	..	..

Barium Nitrate.

The recrystallized substance was dissolved in water and the barium in this solution estimated as the sulphate.

Table XXXIII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	$\mu_v.$	$\alpha.$	$\mu_v.$	$\alpha.$	$\mu_v.$	$\alpha.$
8	177.3	58.3	226.1	59.1	276.2	58.1
32	221.6	72.9	282.0	73.8	344.2	72.4
128	256.4	84.4	325.5	85.1	398.3	83.8
512	283.8	93.4	360.7	94.3	440.7	92.7
2048	299.4	98.5	378.4	99.0	467.0	98.2
4096	303.9	100.0	382.3	100.0	475.5	100.0

Table XXXIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.25	1.83	3.34	1.48
32	4.03	1.82	4.15	1.47
128	4.61	1.80	4.85	1.49
512	5.13	1.81	5.33	1.48
2048	5.27	1.76	5.91	1.56
4096	5.23	1.72	6.21	1.62

Magnesium Nitrate.

The recrystallized salt was dissolved in water and the magnesium in this solution determined as the sulphate. The 0.5 gram-molecular solution was then prepared by volume.

Table XXXV.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	154.5	193.7	234.8
8	193.6	244.5	298.1
32	223.2	283.5	347.4
128	249.2	316.8	390.8
512	266.9	341.6	421.1
2048	278.5	357.0	443.4

Table XXXVI.—*Temperature Coefficients.*

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.61	1.69	2.74	1.41
8	3.39	1.75	3.57	1.46
32	4.02	1.80	4.26	1.50
128	4.51	1.81	4.93	1.56
512	4.98	1.87	5.30	1.55
2048	5.23	1.88	5.76	1.61

Magnesium Sulphate.

The recrystallized salt was dried in a desiccator, then pulverized and the percentage of anhydrous salt in the product determined by ignition.

Table XXXVII.—*Molecular Conductivity.*

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	74.20	92.61	109.2
8	105.7	131.5	155.0
32	140.6	175.7	208.4
128	185.1	234.0	282.7
512	230.7	295.7	358.9
2048	268.4	347.0	427.2
4096	282.0	365.0	446.3

Table XXXVIII.—*Temperature Coefficients.*

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.23	1.66	1.11	1.20
8	1.72	1.63	1.57	1.19
32	2.34	1.66	2.18	1.24
128	3.26	1.76	3.25	1.39
512	4.33	1.88	4.21	1.42
2048	5.24	1.95	5.35	1.54
4096	5.53	1.96	5.42	1.48

Silver Nitrate.

The salt was not recrystallized, but was pulverized and dried thoroughly at 130° for about 12 hours. It was then analyzed and yielded 99.92 per cent. of the theoretical amount of silver chloride.

Table XXXIX.—*Molecular Conductivity and Percentage Dissociation.*

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v	α.	$\mu_v 80°$.
2	99.18	65.4	124.9	65.2	152.2	65.5	177.7
8	119.5	78.8	150.7	78.7	184.8	79.5	215.4
32	133.5	88.0	168.6	88.0	207.7	89.4	243.4
128	142.6	94.0	180.4	94.2	221.4	95.3	262.0
512	148.3	97.8	187.7	98.0	229.0	98.5	...
1024	150.2	99.0	190.1	99.3	230.7	99.3	...
2048	151.7	100.0	191.5	100.0	232.4	100.0	...

Table XL.—*Temperature Coefficients.*

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.71	1.72	1.82	1.46	1.70	1.12
8	2.08	1.74	2.27	1.51	2.04	1.10
32	2.34	1.75	2.61	1.55	2.38	1.15
128	2.52	1.77	2.73	1.51	2.71	1.22
512	2.63	1.77	2.75	1.46	..	..
1024	2.66	1.77	2.71	1.43	..	..
2048	2.65	1.75	2.73	1.43	..	..

Oxalic Acid.

The acid used was recrystallized three times from water. It was then dissolved in water and the strength of this solution was determined by means of potassium hydroxide solution, which had been standardized with sulphuric acid. The latter was estimated as barium sulphate.

The measurement of solutions more dilute than those given in the table was attempted but these were found to be unreliable on account of oxidation brought about by the platinum surface.

Table XLI.—*Molecular Conductivity.*

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	171.8	194.6	211.1
8	211.6	240.1	262.8
32	291.5	333.9	371.7

Table XLII.—*Temperature Coefficients.*

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.52	0.885	1.10	0.565
8	1.90	0.898	1.51	0.629
32	2.83	0.971	2.52	0.755

Malonic Acid.

The acid was recrystallized from a mixture of chloroform and acetone, dried in the air, pulverized and then dried in a desiccator. It showed the correct melting point.

Table XLIII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	31.98	37.38	41.47
16	61.45	71.76	79.73
64	111.8	130.8	145.8
128	148.4	173.8	191.7
512	237.3	277.8	310.9
1024	282.9	331.6	. . .

Table XLIV.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.360	1.13	0.273	0.730
16	0.687	1.12	0.531	0.740
64	1.27	1.14	1.00	0.765
128	1.69	1.14	1.19	0.685
512	2.70	1.14	2.21	0.796
1024	3.25	1.15	. . . .	. . . .

Succinic Acid.

The substance was purified by recrystallizing twice from water. It was dried in the air, pulverized and then dried in a desiccator.

XLV.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
8	9.24	11.00	12.40
32	18.52	21.94	24.71
128	36.00	42.64	48.07
512	69.56	82.36	91.17
1024	92.7	109.9	125.4
2048	123.5	145.8	162.7

Table XLVI.—Temperature Coefficients.

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.117	1.27	0.093	0.845
32	0.228	1.23	0.185	0.843
128	0.443	1.23	0.362	0.849
512	0.853	1.23	0.587	0.713
1024	1.15	1.24	1.03	0.937
2048	1.49	1.21	1.13	0.775

Acetic Acid.

The substance was recrystallized twice by cooling. It was then dissolved in water and the strength of the solution determined as in the case of oxalic acid. From the solution of acetic acid of known strength the 0.5 N solutions were prepared by diluting to a definite volume.

Table XLVII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	2.361	2.720	3.013
8	4.913	5.621	6.240
32	9.79	11.19	12.40
128	19.26	22.04	24.48
512	36.86	41.84	46.31
1024	51.23	58.29	65.2

Table XLVIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.0239	1.01	0.0195	0.717
8	0.0472	0.961	0.0413	0.735
32	0.0933	0.953	0.0807	0.721
128	0.185	0.960	0.163	0.740
512	0.332	0.901	0.298	0.712
1024	0.471	0.919	0.461	0.791

Benzoic Acid.

The substance was purified by recrystallizing twice from water and then dried in a desiccator. It showed the correct melting point.

Table XLIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
64	25.48	29.46	32.21
128	35.44	40.81	45.56
512	67.10	77.63	82.90
1024	89.19	103.4	113.5
2048	117.1	135.6	148.2

Table L.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.265	1.04	0.183	0.621
128	0.358	1.01	0.317	0.777
512	0.702	1.05	0.351	0.452
1024	0.947	1.06	0.673	0.651
2048	1.23	1.05	0.840	0.619

o-*Phthalic Acid.*

The acid was recrystallized twice from water, dried, pulverized and allowed to stand in a desiccator over sulphuric acid.

Table LI.—*Molecular Conductivity.*

V.	μv 35°.	μv 50°.	μv 65°.
32	71.4	82.1	90.5
64	96.2	110.8	122.8
128	128.2	147.7	163.9
512	213.3	246.9	271.5
1024	258.6	300.3	336.3
2048	301.9	351.5	394.3

Table LII.—*Temperature Coefficients.*

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.713	0.999	0.560	0.682
64	0.973	1.01	0.800	0.722
128	1.30	1.01	1.08	0.731
512	2.24	1.05	1.64	0.664
1024	2.78	1.07	2.40	0.799
2048	3.31	1.10	2.85	0.811

Salicylic Acid.

The acid was recrystallized twice from water and after drying was pulverized. It was then dried thoroughly in a desiccator over sulphuric acid. It was weighed directly in making the solutions.

Table LIII.—*Molecular Conductivity.*

V.	μv 35°.	μv 50°.	μv 65°.
64	94.27	111.3	124.8
128	126.1	148.8	166.5
512	210.3	248.0	276.8
1024	253.3	299.0	335.4
2048	294.5	348.8	387.0

Table LIV. *Temperature Coefficients.*

V.	35° to 50°.		50° to 65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
64	1.14	1.21	0.900	0.809
128	1.51	1.20	1.18	0.793
512	2.51	1.19	1.92	0.774
1024	3.05	1.20	2.43	0.813
2048	3.62	1.23	2.55	0.731

It was pointed out some time ago[1] that the chief factor in conditioning the increase in the conductivity of electrolytes with rise in temperature is *the increase in the velocities with which the ions move.*

There are a number of factors determining the velocity with which an ion moves through a solution of an electrolyte. Assuming a constant driving force the velocity is conditioned chiefly by the viscosity of the medium surrounding the ion and through which it moves, and by the size and *mass* of the ion. With rise in temperature the driving force would increase, the viscosity of the medium diminish, and both of these factors would increase the velocity with which the ions move.

Another factor of even greater importance as conditioning the effect of temperature on the velocity of the ion is *the change in the mass of the ion with change in temperature, the hydration or solvation of the ion decreasing with rise in temperature.*

The hydrates or solvates surrounding the ions are unstable— the higher the temperature the less complex the hydrate. The smaller the number of molecules of water in combination with the ion, the smaller the mass of the ion, and the less its resistance in moving through the solvent. Consequently, rise in temperature will cause the ion to move faster through the solvent.

If the factor of diminishing complexity of the hydrate with rise in temperature plays a prominent part in determining the large temperature coefficient of conductivity, we should be able to establish relations at the higher analogous to those at the lower temperatures.

We shall now see whether the relations between temperature coefficients of conductivity and hydration that were found to hold between 0° and 35° hold also between 35° and 65°.

From the following tables the sulphates are omitted, both those that crystallize with much water and are, therefore, largely hydrated in solution, and those that crystallize with only a small amount of water and whose solutions represent only slight hydration. This is done because the sulphates

[1] THIS JOURNAL, **35**, 445 (1906).

are largely polymerized in aqueous solutions, and, therefore present irregularities to any relation that can be pointed out.

Table LV.—Substances with Small Hydrating Power.

	Temperature coefficients in conductivity units.			
	35° to 50°.		50° to 65°.	
	$V = 2.$	$V = 2048.$	$V = 2.$	$V = 2048.$
Sodium chloride.........	1.87	2.69	1.95	2.92
Sodium bromide........	1.66	2.65	2.10	3.00
Sodium nitrate..........	1.67	2.53	1.73	2.53
Potassium chloride......	2.15	2.97	2.12	3.15
Potassium bromide......	2.13	3.02	2.11	3.13
Potassium nitrate.......	1.87	2.77	1.91	2.91
Potassium acetate.......	1.83	2.41	1.88	2.94
Ammonium chloride.....	2.15	3.09	2.17	3.14
Ammonium nitrate......	1.96	2.81	2.06	3.09
Lithium chloride........	1.69	2.49	1.76	2.74
Silver nitrate...........	1.71	2.65	1.82	2.73

Table LVI.—Substances with Large Hydrating Power.

	Temperature coefficients in conductivity units.			
	35° to 50°.		50° to 65°.	
	$V = 2.$	$V = 2048.$	$V = 2.$	$V = 2048.$
Barium chloride.........	2.95	5.77	2.61	5.53
Barium nitrate..........	..	5.27	..	5.91
Magnesium nitrate.. ...	2.61	5.23	2.74	5.76

The more complex the hydrate, *i. e.*, the greater the number of molecules of water combined with an ion, the greater the *change in the complexity of the hydrate with rise in temperature*.

We should therefore expect to find that *those ions with the largest hydrating power have the largest temperature coefficients of conductivity.*

If we compare the results in Table LVI with those in Table LV we shall find the above conclusion very beautifully confirmed by the facts. The substances in Table LVI have large, those in Table LV relatively small hydrating power. The comparisons are made at volumes 2 and 2048—fairly concentrated and fairly dilute solutions. They are also made over the ranges of temperature 35°–50° and 50°–65°.

A glance at the two tables will show that the temperature coefficients in Table LV are much smaller than those in Table LVI for the same concentrations and temperatures, even taking into account the fact that the substances in Table LVI are ternary, while those in Table LV are binary electrolytes.

If the temperature coefficient of conductivity is chiefly a function of the complexity of the hydrate formed by the ions, then *those substances that have approximately equal hydrating power should have approximately the same temperature coefficients of conductivity.* An examination of the two tables will show that this relation holds. The substances in Table LV all have very small hydrating power, which in general is of the same order of magnitude. It will be seen that the temperature coefficients both for $V = 2$ and $V = 2048$ are of the same order of magnitude at both the lower and the higher temperatures.

In Table LVI a similar relation manifests itself. The temperature coefficients for these substances are of the same order of magnitude at the different volumes and over the two ranges of temperature. These substances all show hydration of the same order of magnitude.

One other relation of importance comes out from a study of the above tables. The complexity of the hydrates at the higher dilution is greater than at the lower—the complexity increasing in general with the dilution, as has been shown by work done in this laboratory. The hydrate being more complex at the higher dilution, the change in the complexity of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity would be greater the more dilute the solution.

An examination of the tables will show that *at the higher dilution the temperature coefficient of conductivity for any given substance is greater than at the lower dilution.*

We can summarize the results thus far obtained between $35°$ and $65°$ in exactly the same way as those obtained between $0°$ and $35°$.[1]

[1] THIS JOURNAL, **35**, 450 (1906).
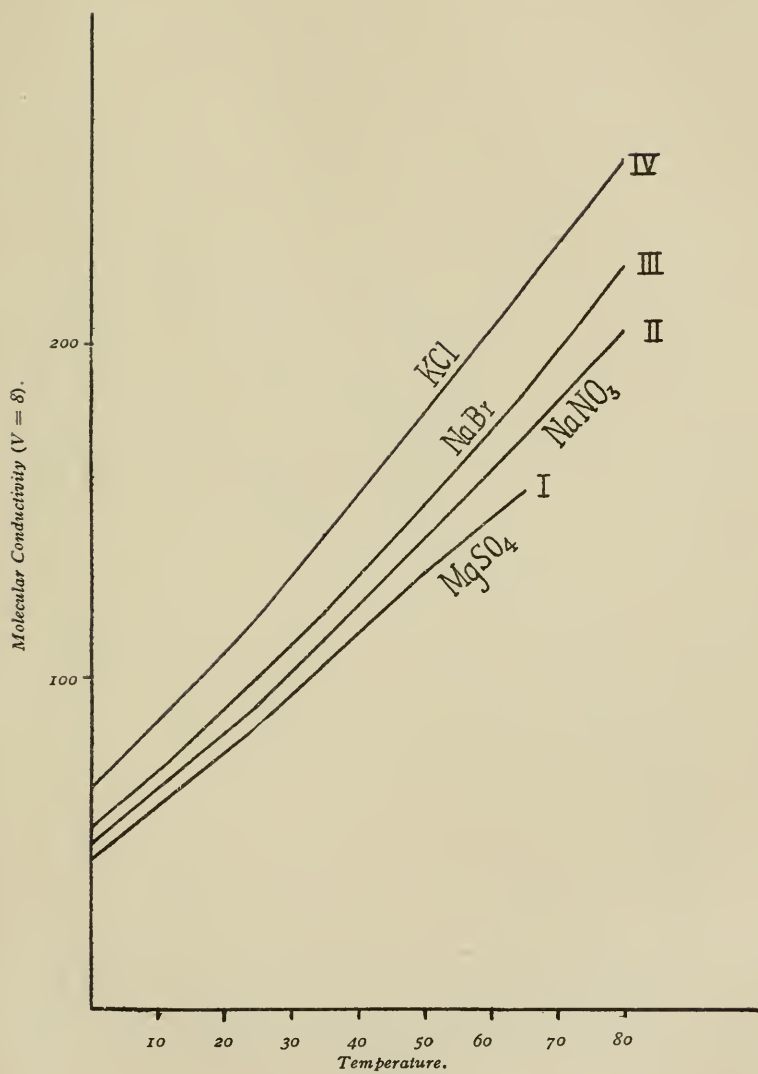
Fig. 1.
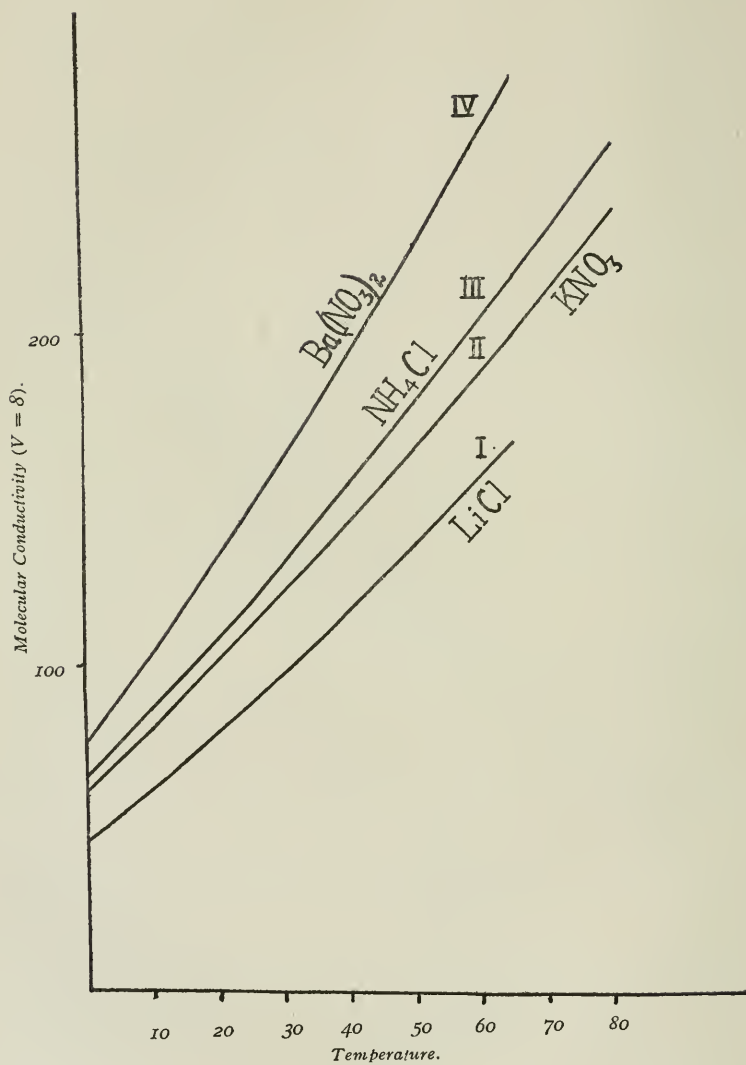
Fig. 2.
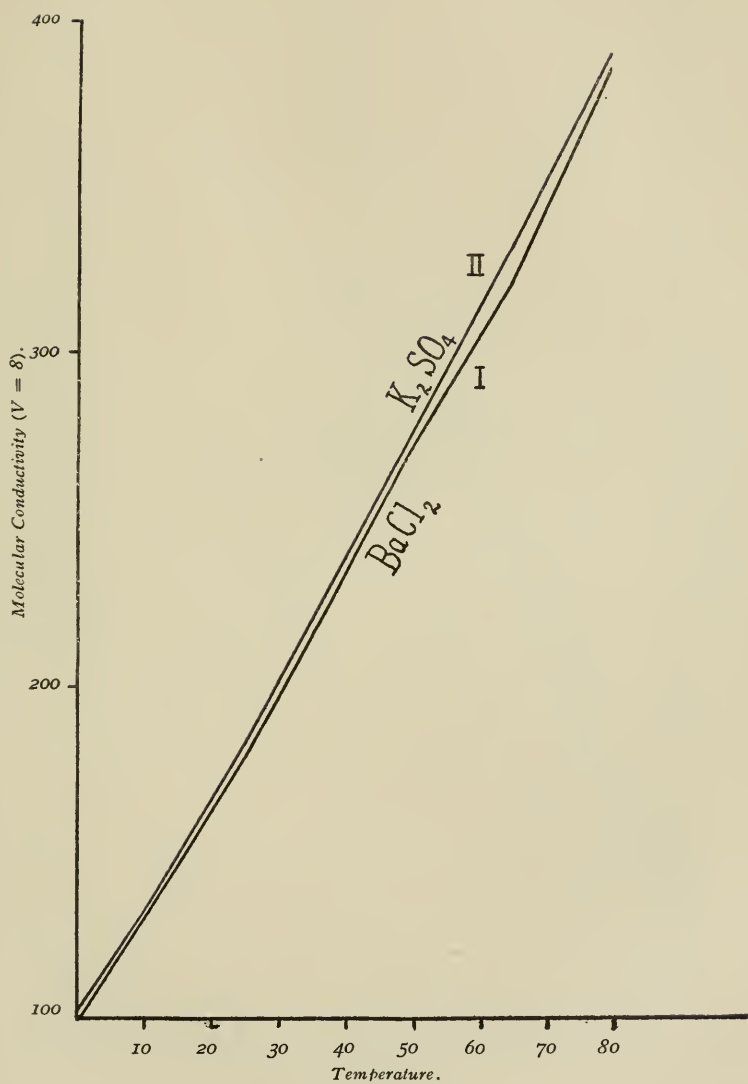
Fig. 3.
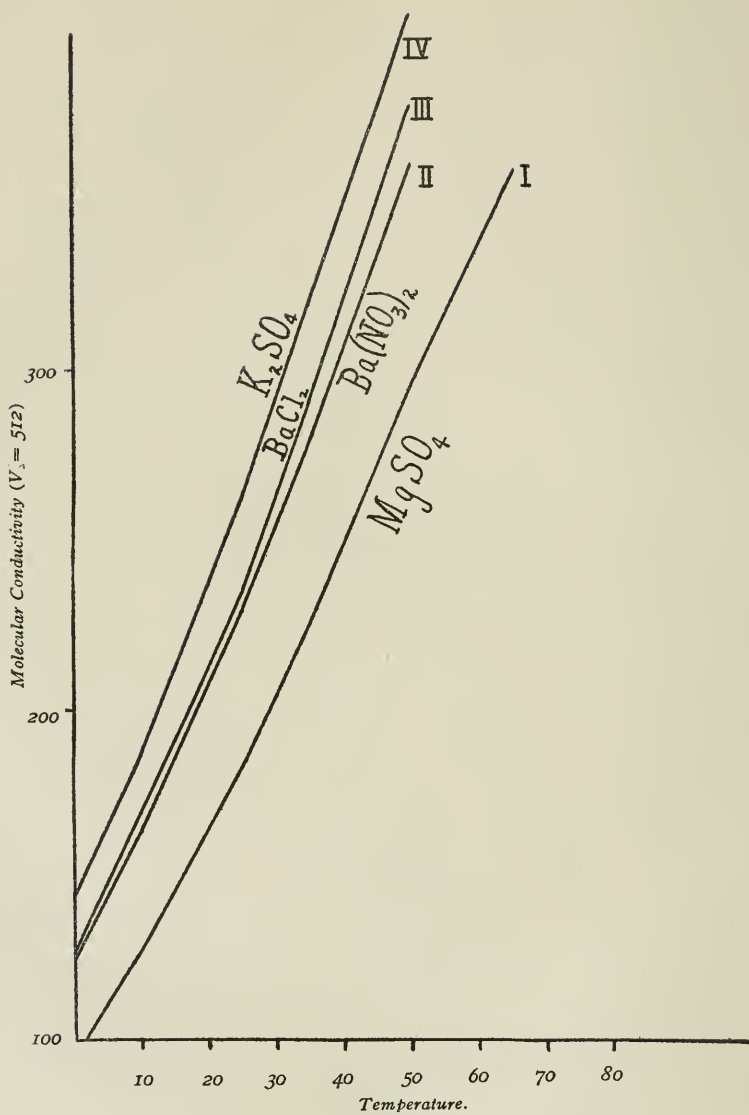
Fig. 4.
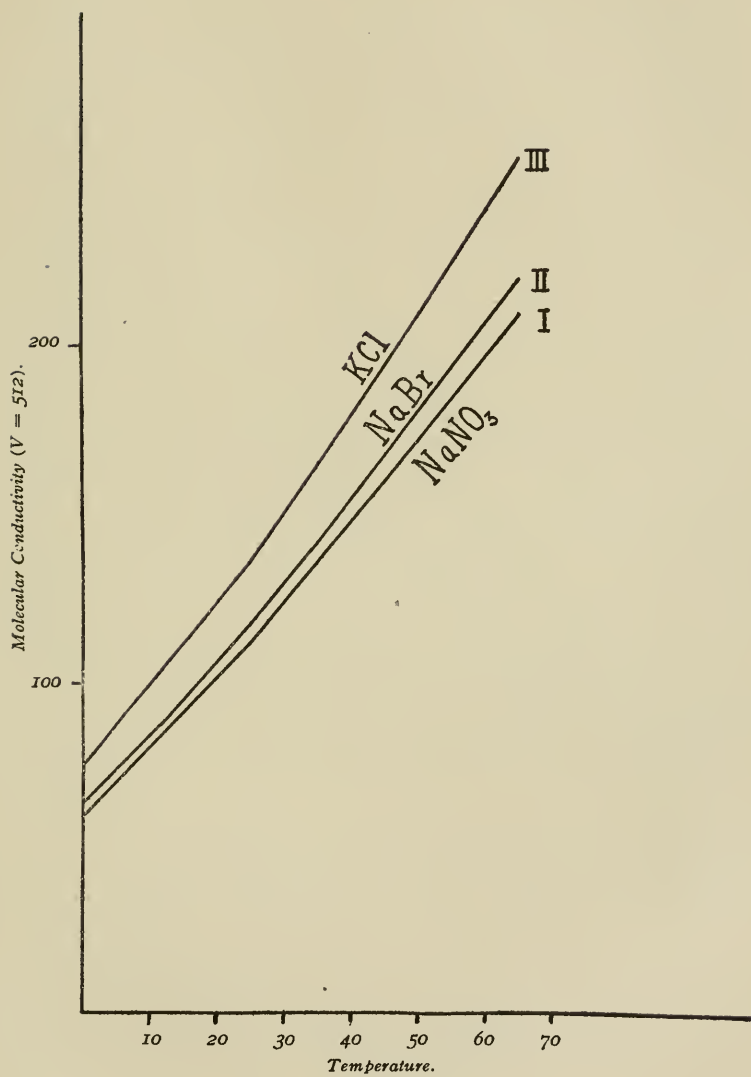
Fig. 5.
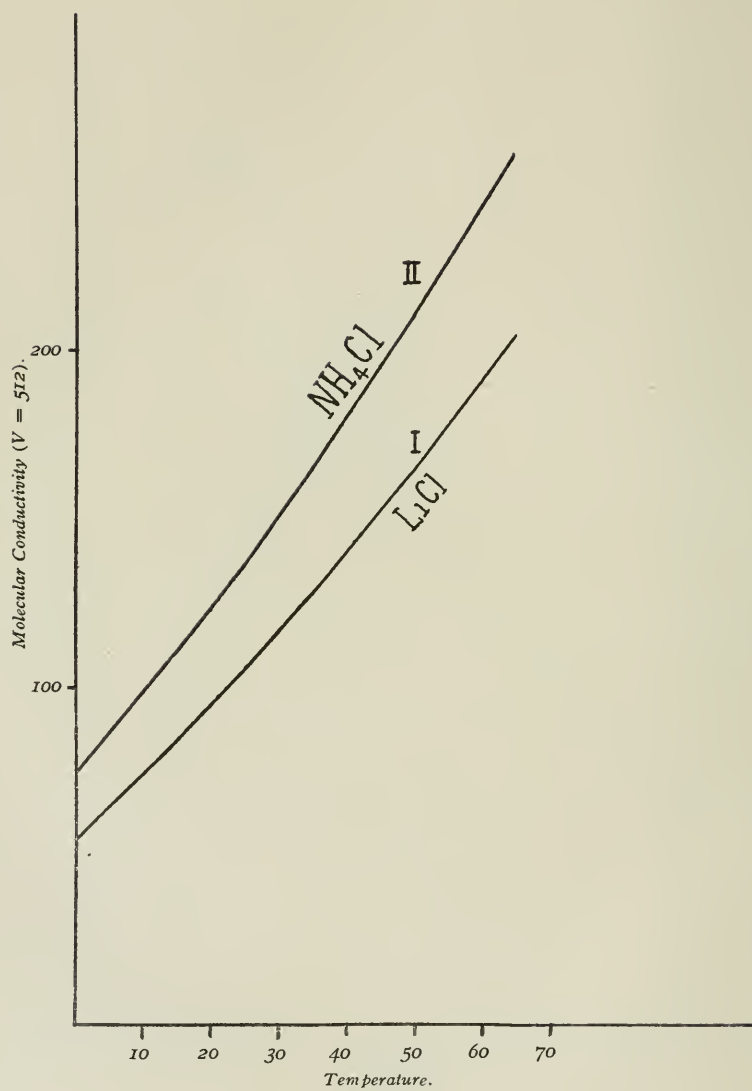
Fig. 6.

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes between 35° and 65° are greater, the more complex the hydrates formed by the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes between 35° and 65° are of the same order of magnitude for those substances having approximately the same hydrating power.

3. The temperature coefficients of conductivity for any given substance increase with the dilution of the solution and the increase is greatest for the substances with the largest hydrating power.

It should be noted that all three of the above conclusions follow of necessity from the assumption that the change in conductivity with change in temperature is due largely to the decreasing complexity of the hydrates formed around the ions as the temperature is raised.

The results for a number of compounds are plotted as curves, the molecular conductivities being ordinates and the abscissas temperature. The curves do not differ greatly from straight lines.

It will be noted that there is a general tendency in the dissociation to decrease slightly with rise in temperature.

Not very much work was done at 80° on account of possible changes in the cell constant, the solubility of the glass, and other sources of error that are liable to come in at the higher temperature.

We are extending this work, which has now been in progress in this laboratory for nine years, to all of the more common electrolytes, inorganic and organic, between 35° and 65°.

Physical Chemical Laboratory,
  Johns Hopkins Univ.,
    June, 1909.

THE ABSORPTION SPECTRA OF SOLUTIONS; A POSSIBLE METHOD FOR DETECTING THE PRESENCE OF INTERMEDIATE COMPOUNDS IN CHEMICAL REACTIONS.

By Harry C. Jones and W. W. Strong.

(The following results were obtained in an investigation that is being carried out with the aid of a Grant from the Carnegie Institution of Washington.)

Jones and Anderson[1] have shown that neodymium chloride has very different absorption bands in water and in alcohol, and Jones and Strong[2] have found a large number of examples illustrating the effect of the solvent on the absorption of light by the dissolved substance. A number of uranous and uranyl salts show different bands in each of the following solvents: water, methyl and ethyl alcohols, glycerol and acetone.

These facts, as has been pointed out, are good evidence for the theory of solvation in terms of which we have been working in this laboratory for a number of years.

It is difficult, not to say impossible, to see how a nonabsorbing solvent can affect the absorption of the dissolved substances unless it enters into some kind of combination with them.

Another set of facts has recently come to light which makes it highly probable that the property of solutions to absorb light can be utilized to detect the presence of intermediate compounds in chemical reactions. Our chemical equations would teach us that when a salt AB is treated with a small amount of a strong acid C, most of the compound AB remains, and a small amount of AC is formed. As the amount of the acid C is increased, the amount of AC increases, until finally we have practically only the compound AC and the free acid B.

Chemists have, however, long suspected that chemical reactions are much more complex than is usually represented

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[1] This Journal, **41**, 163. Carnegie Institution of Washington, Publication No. 110.

[2] This Journal, **43**, 37, 99 (1910).

by our chemical equations. The existence of a number of intermediate products between the initial and final substances seems highly probable. The study of reaction velocities in terms of the law of mass action has shown that many reactions that were regarded as direct and simple are in reality composed of a number of more or less independent reactions. The products of such reactions must, therefore, be much more complex than is usually represented by our equations. The intermediate products formed in such reactions have, in most cases, not been isolated. This is often due to their instability, and also to the lack of sufficiently refined methods for dealing with such problems.

Our work on the power of solutions to absorb light has made it highly probable that intermediate compounds exist in reactions, at least those in which uranium salts are involved.

An aqueous solution of uranyl nitrate has a perfectly definite absorption spectrum. An aqueous solution of uranyl sulphate has likewise a perfectly definite spectrum. If we were to add a small amount of sulphuric acid to a solution of uranyl nitrate and then photograph the absorption spectrum, we would expect to find the bands corresponding to the nitrate coming out strongly, and, simultaneously, those corresponding to the sulphate coming out faintly, since there would be much nitrate and only a little sulphate present. As the amount of sulphuric acid is increased we would expect to find the nitrate bands becoming fainter and fainter and the sulphate bands stronger and stronger, until we should have only the sulphate bands present when practically all of the nitrate had been transformed into sulphate.

The facts are not in accord with these predictions. When sulphuric acid is added to a solution of uranyl nitrate containing free nitric acid (to make the bands sharper) we do not get the absorpton spectrum characteristic either of the nitrate or of the sulphate, but we get a spectrum that is intermediate between the two. Certain of the bands which appeared in the nitrate spectrum are shifted to new positions, the amounts of the shifts depending on the amounts of sulphuric

acid added. As the sulphuric acid present is increased these bands continue to shift until they occupy the positions of the bands of the pure sulphate to which free sulphuric acid had been added.

Even more striking results of the above character were obtained when hydrochloric acid was added to an aqueous solution of uranyl nitrate containing free nitric acid. As the amount of the hydrochloric acid was increased certain of the nitrate bands were greatly shifted, and finally occupied the positions of certain of the chloride bands.

Uranyl nitrate treated with hydrobromic acid behaves in the same manner as when treated with hydrochloric acid.

The most striking example of the above effect, as far as our observations have gone, is the action of nitric acid on an aqueous solution of uranous acetate containing free acetic acid. The addition of more and more nitric acid caused the uranous bands to disappear as the uranous salt passed over into the uranyl condition. At the same time two pairs of the uranyl acetate bands *gradually shifted* their positions and finally united, forming single nitrate bands.

These results are not at all in keeping with the predictions from our chemical conceptions of what takes place in such reactions. The *gradual shift of the bands* when sulphuric acid is added to a solution of uranyl nitrate would indicate the possibility of the formation of a series of more or less unstable systems or compounds, intermedia tein composition between the nitrate and the sulphate. Similarly, when hydrochloric acid is added to an aqueous solution of uranyl nitrate the gradual shift in the bands would indicate that a series of systems or compounds, is formed, the composition depending upon the amount of hydrochloric acid present.

A similar interpretation of the results obtained when nitric acid is added to an aqueous solution of uranous acetate appears to be necessary.

These results from absorption spectra seem to show that in such reactions, at least in those referred to above, we do not have the final product formed at once from the initial substances, as our chemical equations would indicate, but that a

series of more or less unstable intermediate compounds is formed.

It is impossible to say at present of how wide applicability the absorption spectra method is as a means of detecting the presence of intermediate compounds in chemical reactions. For this method to be applicable it is necessary that the solutions of the different salts taking part in the reaction should have different absorption bands, but a number of salts fulfil this condition.

It is now a matter of interest to isolate these intermediate compounds wherever possible, since their existence in solution seems to be indicated by their absorption spectra.

Further work along these lines will be carried out in this laboratory.[1]

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
JANUARY, 1910.

ON THE BEHAVIOR OF THE ORDINARY HEXOSES TOWARDS HYDROGEN PEROXIDE IN THE PRESENCE OF ALKALINE HYDROXIDES, AS WELL AS OF VARIOUS IRON SALTS.

BY H. A. SPOEHR.

The experiments of Nef and his students[2] prove that the various hexose sugars are split in alkaline solution, through formation of 2,3- and 3,4-dienols, into diose, and isomeric trioses and tetroses, which, in the form of dienols, can also

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[1] Since the above note was sent to press the following results have been obtained with salts of neodymium. The different salts of neodymium show, in general, very much the same absorption bands. The absorption spectrum of an aqueous solution of neodymium acetate, however, differs very considerably from that of the chloride, the nitrate or the sulphate.

Spectrograms have therefore been made, showing the changes that take place when different amounts of hydrochloric or nitric acid are added to neodymium acetate. The results were of the same general character as with the uranyl salts. While nitric acid made the bands broad and hazy, hydrochloric acid produced a number of new bands intermediate in position between those of the acetate and the chloride. We interpret these results as we interpreted those with the uranyl salts. A number of intermediate systems or compounds between the acetate and the chloride are formed.

[2] Ann. Chem. (Liebig), **357**, 214–312. Anderson: THIS JOURNAL, **42**, 401–430.

give, by further dissociation, hydroxymethylene or formaldehyde molecules.[1] We know further through the work of Lobry de Bruyn and Ekenstein[2] on *d*-galactose and *d*-glucose, respectively, that certain isomeric aldo- and 2-ketohexoses are reciprocally interconvertible in alkaline solution. Nef has shown[3] that this must be due to an intermediate formation of 1,2-dienols, which can then add water in various ways to give the isomeric sugars actually obtained; he concluded further,[4] from theoretical considerations, that glutose and galtose, obtained by Lobry de Bruyn and Ekenstein[5] from *d*-glucose and *d*-galactose by means of calcium as well as lead hydroxide, must each consist of a mixture of two isomeric 3-ketohexoses, to which he therefore gave the names α- and β-*d*-glutose and α- and β-*d*-galtose, respectively. My work (see below) proves the correctness of the conclusion of Nef with reference to the constitution and nature of the sugars last named, so that it is now certain that glutose and galtose are isomeric 3-ketohexose sugars of the dextro series. Furthermore, since the *d*-glutose and *d*-galtose sugars are not mutually interconvertible by means of caustic alkalies and also never give the corresponding members of the laevo series under the conditions named, Nef[6] concluded that the 3-ketohexoses must give 2,3-dienols by preference and, further, that the moment 3,4-dienol formation takes place, a spontaneous splitting into two molecules of glyceric aldehyde must result. He concluded finally also that the conversion of aldo- and 2-ketohexoses into the isomeric 3-ketohexoses was a nonreversible process,[7] and explained this on the assumption that the 2,3-dienols must add water so as to give 3-ketohexoses only:

$$CH_2OHC(OH)=C(OH)CHOHCHOHCH_2OH + HOH \longrightarrow$$
$$CH_2OHCHOHC(OH)_2CHOHCHOHCH_2OH \longrightarrow$$
$$CH_2OHCHOHC(=O)CHOHCHOHCH_2OH + H_2O.$$
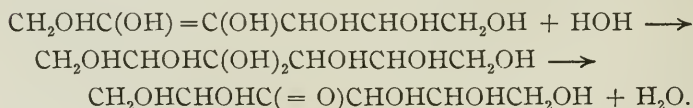
[1] Ann. Chem. (Liebig), **335**, 195, 282.
[2] Rec. Trav. Chim., **14**, 158, 203: **15**, 92; **16**, 257; **19**, 1.
[3] Ann. Chem. (Liebig), **357**, 294.
[4] *Ibid.*, **357**, 297.
[5] Rec. Trav. Chim., **16**, 258, 269, 274.
[6] Ann. Chem. (Liebig), **357**, 299.
[7] *Ibid.*, **357**, 297.

Dr. Nef tells me that he now considers this conclusion, which was based entirely upon the work of the Dutch chemists named above—namely, that glutose and galtose cannot be converted back into 2-keto and aldohexose sugars by alkalies—very improbable. It seems to him that the only rational way in which to explain the reciprocal transformation (by alkaline hydroxides) of *d*-fructose and pseudofructose, on the one hand, and of *d*-tagatose and *l*-sorbose, on the other hand, is on the basis that the 2,3-dienol common to the 2- and 3-keto-hexoses under consideration,

$$CH_2OHC(OH)=C(OH)\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{\rule{0pt}{0pt}}}\!\!-\!\!-\!\!\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{\rule{0pt}{0pt}}}CH_2OH, \text{ and}$$
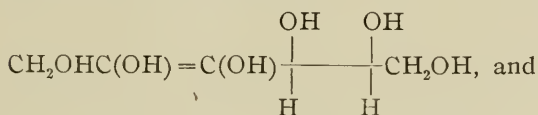
2,3-Dienol common to *d*-fructose, pseudo-
fructose and α- and β-*d*-glutose.

$$CH_2OHC(OH)=C(OH)\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{\rule{0pt}{0pt}}}\!\!-\!\!-\!\!\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{\rule{0pt}{0pt}}}CH_2OH,$$
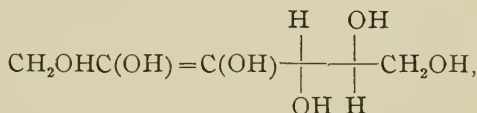
2,3-Dienol common to *d*-tagatose, *l*-sorbose,
and α- and β-*d*-galtose.

must add water to the ethylene grouping so as to give *all* the isomeric 2- and 3-ketohexoses under consideration; this naturally means, therefore, that the 3-ketohexoses must go back in the presence of alkaline hydroxides (aside from their splitting into diose, triose and tetrose mentioned above) into 2-keto- and aldohexose sugars of the *corresponding* dextro series; it is, however, exceedingly probable that these last named sugars (in all, six of one series) are finally present in relatively far smaller amounts than the main components—the two isomeric 3-ketohexose sugars. This would explain why Lobry de Bruyn and Ekenstein were never able to prove that glutose or galtose go back with alkalies into 2-keto- and aldohexoses; it would, in fact, be impossible to establish this experimentally by any methods yet known.

Turning now to the final explanation of the action of Fehling's solution on sugars, as given by Nef in the recent thesis

of Anderson,[1] it will at once be seen how beautifully this is in harmony with the conclusions just presented. *d*-Mannose, *d*-glucose, and *d*-fructose all give the same oxidation products in the presence of sodium and cupric hydroxides, namely, carbon dioxide, formic, glycollic, *d,l*-glycerinic acid, *l*-threonic and *d*-erythronic lactones (trihydroxybutyric acids) and the three hexonic acids—*d*-mannonic, *d*-gluconic and α-hydroxy-methyl-*d*-arabonic acid. The formic acid obviously comes from the oxidation of the hydroxymethylene molecules, whereas the diose, triose and *d*-erythrose (present as dissociation products of the 2,3- and 3,4-dienols of the hexoses under consideration) as well as the aldo-, 2- and 3-ketohexoses at first present or subsequently formed in the alkaline solution, are oxidized to their corresponding osones, and then give by a benzilic acid rearrangement (asymmetric in part or entirely) the various acids just named.

When *d*-galactose (or *d*-tagatose or *d*-talose) are oxidized with Fehling's solution the same products and in approximately the same ratio are obtained as with the members of the *d*-glucose series, excepting that in place of the three hexonic acids mentioned above we now obviously obtain *d*-galactonic, *d*-talonic (from 1,2-galactosone), and α-hydroxymethyl-*d*-lyxonic acid (from the 2,3-galtosone) by an asymmetric benzilic acid rearrangement.

Since preliminary experiments by Dr. Nef and his students[2] with hexoses had shown that these sugars, when oxidized in the presence of sodium, potassium, barium or calcium hydroxide by air, or freshly precipitated oxide of mercury, give practically the same oxidation products and in the same ratio as with Fehling's solution, I began experiments, at Dr. Nef's suggestion and under his guidance, on the oxidation of *d*-glucose and *d*-galactose in alkaline solutions in the presence of hydrogen peroxide. It was at first expected, especially also because of the preliminary observations published by Buchner, Meisenheimer and Schade,[3] that besides much formic acid the same hydroxy acids would be obtained as when air, oxide

[1] This Journal, **42**, 403.
[2] *Ibid.*, **42**, footnote, p. 406.
[3] Ber. d. chem. Ges., **39**, 4217; **41**, 1009, footnote.

of mercury, or copper, was present besides the caustic alkali. There was, however, this remarkable difference: *d*-glucose and *d*-fructose each gave only four oxidation products, namely, small amounts of carbon dioxide, glycollic, and α-hydroxy-methyl-*d*-arabonic acids; and the main reaction product was formic acid, 48.3 to 65.3 per cent. of the calculated possible amount. With *d*-galactose still smaller amounts of the three corresponding acids, carbonic, glycollic and α-hydroxymethyl-*d*-lyxonic acids, were obtained; in this case over 80 per cent. of the sugar was oxidized to formic acid! We have here, therefore, remarkable instances of what is temporarily called selective oxidation. As stated above, an alkaline solution of *d*-glucose slowly gives the following 8 hexose sugars: *d*-glucose, *d*-mannose, *d*-fructose, α- and β-*d*-glutose, *d*-allose, *d*-latose, and *d*-pseudofructose; the solution contains in addition, through spontaneous dissociation of the 2,3- and 3,4-dienols of these hexoses, formaldehyde, diose, triose, and tetrose sugars. The situation in the case of *d*-galactose is entirely similar except that we must substitute the eight members of the *d*-galactose series, *i. e.*, certain aldo- and 2- and 3-keto-hexoses[1] for those members of the *d*-glucose series just named.

In the presence of the hydrogen peroxide, therefore, the only sugars present in the alkaline solution which are actually selectively oxidized are: (1) formaldehyde, hydroxymethylene, which can be present only in marvellously small concentration, and yet is the source of all the formic acid actually obtained; (2) glycollic aldehyde, which is transformed in part into glycollic acid and in part through an intermediate formation of glyoxylic acid into carbon dioxide and formic acid; (3) α- and β-*d*-glutose,

$$\text{CH}_2\text{OH}\overset{\overset{\displaystyle \text{OH}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{}}\text{CO}\overset{\overset{\displaystyle \text{OH}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{}}\overset{\overset{\displaystyle \text{OH}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{}}\text{CH}_2\text{OH} \text{ and}$$

$$\text{CH}_2\text{OH}\overset{\overset{\displaystyle \text{H}}{|}}{\underset{\underset{\displaystyle \text{OH}}{|}}{}}\text{CO}\overset{\overset{\displaystyle \text{OH}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{}}\overset{\overset{\displaystyle \text{OH}}{|}}{\underset{\underset{\displaystyle \text{H}}{|}}{}}\text{CH}_2\text{OH},$$
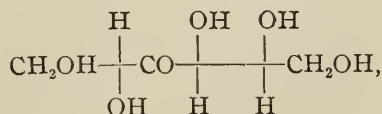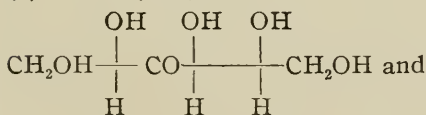
[1] Nef: Ann. Chem. (Liebig), **357**, 295.

which give the same 2,3-glutosone,

$$CH_2OH - \overset{\|}{\underset{O}{C}} - \overset{\|}{\underset{O}{C}} \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} CH_2OH,$$
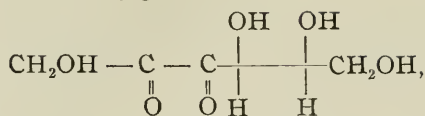
and this by an *entire* asymmetric benzilic acid rearrangement[1] then gives *only* α-hydroxymethyl-*d*-arabonic acid,

$$COOH \overset{HOH_2C}{\underset{OH}{|}} \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} CH_2OH;$$ the α- and β-galtose
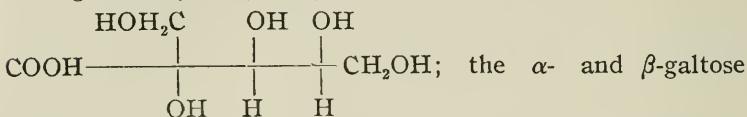
formed from *d*-galactose give, by an entirely analogous reaction, α-hydroxymethyl-*d*-lyxonic acid,
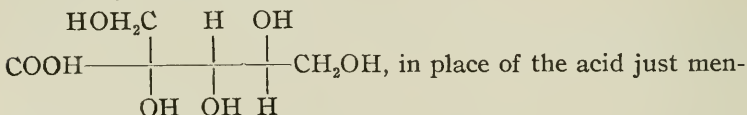
$$COOH \overset{HOH_2C}{\underset{OH}{|}} \overset{H}{\underset{OH}{|}} \overset{OH}{\underset{H}{|}} CH_2OH,$$ in place of the acid just men-

tioned.

The first case of selective oxidation of sugars observed in this laboratory was by Miss Denis.[2] She found that acetol, when oxidized in alkaline solution in the presence of mercuric oxide, gives practically *d,l*-lactic acid only, whereas, when silver oxide is present besides the caustic alkali, acetic and formic acids are the only oxidation products obtained. Now it is clear from Nef's work that an alkaline solution of acetol (= methyldiose) contains the following substances: acetol, $CH_3-CO-CH_2OH$, and its dienol, $CH_3COH=CHOH$; acetylmethylene, $CH_3CO-CH{\geqslant} + H_2O \rightleftarrows CH_3-CO-CH_2OH$; hydroxymethylene, ${\leqslant}CHOH$, and hydroxyethylidene, $CH_3COH{\geqslant}$ —the dissociation products of the 1,2-dienol of acetol. In the case of silver oxide, the last two named substances are therefore obviously the only two products oxidized, whereas with the oxide of mercury, the acetylmethylene molecules are selectively chosen and converted into pyruvic aldehyde by oxidation, and this is then at once transformed by a benzilic acid rearrangement into *d,l*-lactic acid.

[1] Nef: Ann. Chem. (Liebig), **298**, 305.
[2] This Journal, **38**, 579.

EXPERIMENTAL PART.

Part I. Behavior of d-*Glucose*, d-*Fructose* and d-*Galactose* towards Alkaline Hydrogen Peroxide.

a. Quantitative Determination of the Amounts of Carbon Dioxide and of Formic Acid Formed in the Oxidation.—Two grams of sugar were dissolved in 80 cc. of three per cent. solution of hydrogen peroxide[1] (6.5 molecules); no action was ever observed to take place under these conditions even on long standing. The colorless mixture was at once poured into a solution of 5.62 grams potassium hydroxide (9 molecules) in 100 cc. water, and diluted with water so that the initial concentration of the alkali was approximately half normal; the presence of a soda-lime tube prevented the access of carbon dioxide from the air and permitted the escape of hydrogen. The solution always remained absolutely colorless— in marked contrast to the strong coloration noticed when sugar solutions are allowed to stand alone with soluble alkaline hydroxides; there was no appreciable rise in temperature, but a noticeable difference in the speed of oxidation of d-fructose, d-glucose and d-galactose was observed—the reaction, proceeding most rapidly with the last named sugar, and far more slowly with d-glucose. This must finally be the sole basis for explaining (especially in the case of d-glucose and d-fructose) the remarkable differences in the relative amounts of the four oxidation products observed. It is therefore probable that a difference in the ratio of the four oxidation products formed would also be observed by simply varying the concentrations in the oxidation of the same sugar, but I have not as yet carried out any experiments to test this point. After allowing the above-mentioned solution to stand for two days in the case of d-galactose, and for three days in the case of the two other sugars named, no more sugar was found present, as shown by testing with Fehling's solution; the excess of hydrogen peroxide was then destroyed by adding a little platinum black and stirring violently. The amount of carbon dioxide, as well as of formic acid, formed in the oxida-

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[1] The exact strength of this reagent was always determined just before using by titration with permanganate. Cf. Classen: Quant. Anal., II, 211.

tion, was then determined as follows: the calculated amount of aqueous hydrogen chloride was first added, by means of a separatory funnel, to the alkaline solution in a flask, which was connected with a reflux condenser and a series of cylinders containing saturated solutions of barium hydroxide. Air free from carbon dioxide was continually drawn through the acidified solution and finally the flask was heated in a bath kept between 110°–120° for one hour, to ensure the complete expulsion of carbon dioxide. The barium carbonate precipitated in the cylinder was well washed, dried at 100°, and then weighed. A correction was, of course, made for the amount of carbon dioxide present in the potassium hydroxide used, as determined by a blank experiment. In order to determine the formic acid remaining in the aqueous solution, it was removed, together with the water, by distilling under 15–30 mm. pressure from a flask provided with a Kjeldahl bulb to prevent volatilization of glycollic acid, heating finally on a boiling water bath, and then redissolving the residue in a small amount of water and repeating the distillation. The aqueous distillates proved to be free from traces of hydrogen chloride and were then made up to a definite volume; the amount of the formic acid present in an aliquot portion was then determined by titration with 0.1 N alkali as well as by oxidation to carbon dioxide with 0.1 N permanganate.[1] Since the two methods gave results which agreed perfectly, it is certain that no acid other than formic acid could have been present. Oxalic acid was also looked for with especial care in the nonvolatile salt residue, but always with negative results. Herewith is given a summary of the quantitative results obtained in the oxidation of the three sugars named:

2 grams of *d*-fructose gave 0.105 gram CO_2, *i. e.*, 3.58 per cent.; and 1.48 grams formic acid, *i. e.*, 48.3 per cent. of the amount theoretically possible.

2 grams of *d*-glucose gave 0.103 gram CO_2, *i. e.*, 3.51 per cent.; and 2.00 grams formic acid, *i. e.*, 65.3 per cent.

2 grams of *d*-galactose gave 0.143 gram CO_2, *i. e.*, 4.65 per cent.; and 2.46 grams formic acid, *i. e.*, 80.2 per cent.

[1] H. C. Jones: This Journal, **17**, 539.

b. *The Nonvolatile Acids, Glycollic and α-Hydroxymethyl-*d-

$$\text{arabonic Acid, } \quad \text{COOH}\underset{\overset{|}{\underset{\text{OH}}{}}}{\overset{\overset{\text{HOH}_2\text{C}}{|}}{}}\underset{\overset{|}{\underset{\text{H}}{}}}{\overset{\overset{\text{OH}}{|}}{}}\underset{\overset{|}{\underset{\text{H}}{}}}{\overset{\overset{\text{OH}}{|}}{}}\text{CH}_2\text{OH, } \textit{from } \text{d-}\textit{Fruc-}$$

arabonic Acid, COOH——————CH$_2$OH, *from* d-*Fruc-*
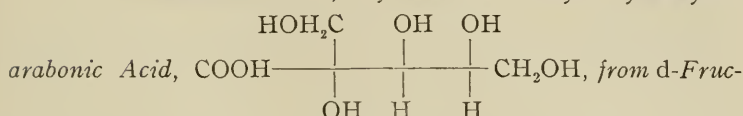
tose and d-*Glucose.*—In order to determine the nature of the nonvolatile acids left with the salt residue after the removal of the water and volatile acids by distillation, as stated above, at least 100 grams of sugar had to be taken for oxidation (usually in four operations with 25 grams). The reactions had invariably proceeded to completion after standing three days at ordinary temperature, and it was now found more convenient to get rid of the hydrogen peroxid still present by longer standing or more rapidly by simply heating for a short time. It was furthermore also found advisable to add subsequently a slight excess over the calculated amount of hydrogen chloride, and then to remove the water and volatile acids, including also a part of the excess of hydrogen chloride, by distilling at 15–30 mm. as before, heating finally on a boiling water bath; if only the calculated amount of hydrogen chloride is added some potassium glycollate, melting at 149°, and supposed at first to be *d*-mannonic lactone, is always obtained after extracting the salt residue thoroughly with absolute alcohol and subsequent concentration of the alcoholic filtrates. I obtained, for example, by proceeding in this way with 100 grams *d*-fructose, a total of 19.42 grams of potassium glycollate (in four crops) melting at 147°–149° and crystallizing in glistening needles. These gave, on treatment with an excess of hydrogen chloride, etc., and subsequent extraction of the salt residue with ether, 13.2 grams of crude glycollic acid melting from 72°–74°. Its identity with glycollic acid was proved, first, by titration with 0.1 N potassium hydroxide: 0.3534 gram in 50 cc. water required for neutralization 45.4 cc. 0.1 N potassium hydroxide; second, by conversion into the phenylhydrazine salt, described by Nef:[1] 0.4 gram in 1 cc. alcohol and 0.5 gram phenylhydrazine yielded 0.7 gram of the glistening white plates melting at

[1] Ann. Chem. (Liebig), **357**, 223.

100°; and third, by transformation into the characteristic calcium salt.

The original alcoholic filtrate from the 19.42 grams of potassium glycollate mentioned above was found, after removal of the alcohol by distillation under diminished pressure, to contain a large amount of gum which was first treated with a small amount of hydrogen chloride, etc., and then separated from a small amount of chloride of potassium by dissolving in a little absolute alcohol. The clear light brown gum finally obtained weighed 20 grams and was then resolved by digestion with ether and with acetic ether: (1) Into a portion, A, soluble in ether, 3.4 grams; (2) into a portion, B, soluble in much acetic ether, 12.93 grams; and (3) into an insoluble portion, C, 3.47 grams, which still contained some tar and potassium chloride, since on acylation with 11 cc. acetic anhydride, and subsequent hydrolysis of· the acylated material soluble in ether, only 2.31 grams of gum were recovered. Gum A, treated with an excess of powdered strychnine, etc., gave a total of 12.9 grams of crude glycollic strychnine,[1] melting at 180°–190° and decomposing at 235°, from which 8.25 grams of crystallized calcium glycollate,

$$Ca(C_2H_3O_3)_2.4H_2O,$$
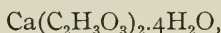
corresponding to 2.4 grams of glycollic acid, were finally obtained. Gum B, after titration of a small portion with tenthnormal alkali, which gave results agreeing with those calculated for trihydroxybutyric lactone, was shown, by conversion of the main portion into brucine salts, to consist only of a mixture of glycollic acid and a new hexonic acid, α-hydroxymethyl-*d*-arabonic acid, According to unpublished observations of Nef, brucine glycollate contains crystal water, melts at 82° (or after loss of crystal water at 120°), and is very soluble in cold absolute alcohol; the brucine salt of the new hexonic acid, on the other hand, melts, according as it contains or loses its crystal water, within the range of 168°–188°, is sparingly soluble in cold absolute alcohol, and separates out from this solvent in the anhydrous form in opaque nodules looking much like brucine *d*-gluconate, and melting at 187°–

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[1] Ann. Chem. (Liebig), **357**, 238.

188°. When crystallized from 3 parts of alcohol and one-third part of water, the salt separated out in transparent flat plates melting from 167°–170°; these lose, on drying for a week over sulphuric acid *in vacuo*, a small and indefinite amount of water, but by this process the melting point invariably is raised to 186°–188°. The salt can also be crystallized from a small amount of water. By fractional crystallization of the brucine salts obtained from the gums B and C, separation of these into high (above 160°) and low (120°–140°) melting, and gummy salts, conversion of the gummy and low melting salts into the free acids, and subsequently into the corresponding strychnine salts, and then separation of the difficultly soluble strychnine glycollate from the easily soluble strychnine salt of α-hydroxymethyl-*d*-arabonic acid by crystallization from alcohol, I finally obtained in all from gums A, B and C, 34.7 grams of pure anhydrous brucine α-hydroxymethyl-*d*-arabonate melting from 185°–188°, with $[\alpha]_D^{20} = -25°.94$; this corresponds to 10.34 grams of α-hydroxymethyl-*d*-arabonic lactone. The total amount of glycollic acid obtained from these fractions was only 3.5 grams, which, with the 13.2 grams previously obtained from the potassium salt, makes a total of 16.7 grams of this acid from 100 grams *d*-fructose.

c. d-*Glucose.*—Dextrose and laevulose each give the same four acids by oxidation under the conditions named, but there is a very remarkable difference in the relative amount of these products formed which can be due only to a difference in the speed of oxidation in the two cases, the oxidation proceeding, under the same conditions of concentration, noticeably faster in the case of *d*-fructose. Four portions of twenty-five grams *d*-glucose, melting at 148°–149°, were dissolved each in 865 cc. 3 per cent. hydrogen peroxide (5.5 molecules) and poured into a normal solution of potassium hydroxide containing 70 grams of the alkali (9 molecules), as described above. No sugar was left after standing 65 hours, and on getting rid of the oxidizing agent, adding an excess of hydrogen chloride, etc., an acetic ether extract containing 25.87 grams nonvolatile acids was finally obtained. These were

resolved by two-fold fractional crystallization of the brucine and strychnine salts, as described above under *d*-fructose, into 23.07 grams practically pure glycollic strychnine, corresponding to 4.3 grams free glycollic acid, and into 62.1 grams pure α-hydroxymethyl-*d*-arabonic brucine melting at 183°–188° with $[\alpha]_D^{20}$ = —25°.7, corresponding to 18.78 grams of α-hydroxymethyl-*d*-arabonic lactone. This result proves in a most decisive manner that only these two acids could possibly have been present. Especially worthy of notice is the fact that here, in marked contrast to the experiments with *d*-fructose, the amount of glycollic acid formed is exceedingly small; furthermore, *d*-glucose, although its transformation into α- and β-*d*-glutose involves an intermediate formation of laevulose, actually gives a somewhat larger yield of α-hydroxymethyl-*d*-arabonic lactone than does *d*-fructose itself.

In order, therefore, to obtain a sufficiently large amount of the new hexonic acid for an exhaustive study, and especially for the determination of its constitution, a second series of oxidation experiments with eight portions of 25 grams of *d*-glucose (*i. e.*, with 200 grams sugar in all) was carried out under practically the same conditions as those just described. The nonvolatile acids were resolved into an ether extract, 9.7 grams gum, which consisted mainly of glycollic acid, and into an acetic ether extract containing 44.5 grams gum. The latter, after long digestion in aqueous solution with an excess of powdered calcium carbonate and finally with a small amount of powdered quicklime (to ensure complete transformation of the lactone into the salt), gave, on concentration of the aqueous solution, 37.3 grams of the very characteristic calcium α-hydroxymethyl-*d*-arabonate, $Ca(C_6H_{10}O_7)_2.5H_2O$; a large portion of this was used in the oxidation experiment with nitric acid (described below).

On the Properties and Constitution of the New Hexonic Acid Called α-Hydroxymethyl-d-arabonic Acid,

$$\underset{\text{OH}\quad\text{H}\quad\text{H}}{\overset{\text{HOH}_2\text{C}\quad\text{OH}\quad\text{OH}}{\text{COOH}\underline{\hspace{3cm}}\text{CH}_2\text{OH.}}}$$
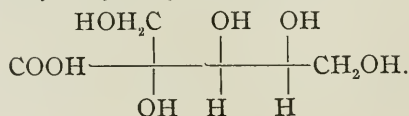
Brucine Salt.—The homogeneous nature of the acid called α-hydroxymethyl-d-arabonic acid was established by a careful study of its crystalline derivatives. The most characteristic of these is perhaps its brucine salt, which separates out very completely on crystallizing the salt from one-third its weight of water and three parts of alcohol; transparent plates are thus obtained which melt between 167° and 170°; these lose a small amount of water on long drying over sulphuric acid *in vacuo* and the melting point is thereby raised to 186°–188°. On crystallizing the anhydrous salt from absolute alcohol heavy opaque nodules are obtained, generally of the same melting point, but in one case I obtained a melting point as high as 200°. The substance, when crystallized from aqueous alcohol and then dried over sulphuric acid *in vacuo* to constant weight, melted somewhere about 186°–188° and then gave a specific rotation $[\alpha]_D^{20} = -25°.7$. (*a*) 1.0096 grams of the anhydrous salt, obtained from d-fructose, in 24.2283 grams water, therefore, $p = 4.00$, $d = 1.012$, gave α in 1 dcm. tube $= -1°.05$, *i. e.*, $[\alpha]_D^{20} = -25°.94$. (*b*) 1.0324 grams anhydrous salt, obtained from d-glucose, dissolved in 23.7041 grams of water, therefore $p = 4.17$, $d = 1.012$, gave α in a 2 dcm. tube $= -2°.16$, *i. e.*, $[\alpha]_D^{20} = -25°.7$. (*c*) 1.0122 grams anhydrous salt from d-glucose, dissolved in 22.6021 grams water, therefore $p = 4.28$, $d = 1.012$, gave α in 2 dcm. tube $= -2°.15$, *i. e.*, $[\alpha]_D^{20} = -25°.7$.

The free lactone was always obtained as a thick viscous gum, the specific rotation of which in 4 per cent. aqueous solution was found to be $+72°.5$; it was made from either the pure brucine or calcium salt by the usual methods. In the case of the brucine salt a hot aqueous solution was digested with an excess of either barium hydroxide or sodium hydroxide, and the precipitated brucine was thereupon separated from the cold solution by filtration, and the small amount yet remaining in solution was removed by extraction with chloroform. The lactone gum, first freed from traces of barium salt or sodium chloride by extraction with acetic ether, etc., was then dissolved in a small amount of water and heated finally under 15–30 mm. pressure in a distilling flask

in a bath kept at 100° for one-half hour. Thus 0.98 gram gum, obtained from the calcium salt, dissolved in 25 cc. water, therefore $p = 3.77$, $d = 1.011$, gave α in a 2 dcm. tube $= +5°.53$, whence $[\alpha]_D^{20} = +72°.5$.

The phenylhydrazide, $C_6H_{11}O_6.NHNHC_6H_5$, separates out almost quantitatively in crystalline needles on letting a solution of the lactone in 2 parts of 80 per cent. alcohol stand with an equal weight of phenylhydrazine for 24 hours at ordinary temperature. It is practically insoluble in absolute alcohol and ether and is therefore obtained sufficiently pure by simply washing with cold alcohol until snow-white. On recrystallizing 1.67 grams of the substance thus obtained from 30 cc. hot water 1.25 grams separated out, on standing overnight, in glistening needles melting from 212°–215°. A determination of the specific rotation of three different preparations of the substance in about 2 per cent. aqueous solution gave the following results: (*a*) 0.9625 gram (from *d*-fructose) in 48.7420 grams water, therefore $p = 1.93$, $d = 1.003$, gave $\alpha = -0°.52$ in a 2 dcm., tube whence $[\alpha]_D^{20} = -13°.42$. (*b*) 0.5079 gram substance (from *d*-glucose) melting at 210°–215° and 24.2031 grams water, therefore $p = 2.05$, $d = 1.003$, gave α in 1 dcm. tube $= -0°.24$, whence $[\alpha]_D^{20} = -12°.1$. (*c*) 0.3290 gram salt (from *d*-glucose) melting at 214° and 14.7014 grams water, therefore $p = 2.18$, $d = 1.003$, gave α in 2 dcm. tube $= -0°.61$, whence $[\alpha]_D^{20} = -13°.9$.

The analyses given below were carried out by José I. Rosario, who obtained the substance as one of the oxidation products of *d*-fructose in alkaline solution by air.

0.2635 gram substance gave 22.8 cc. N_2 at 20°.9 and 744.1 mm. pressure.

0.2025 gram substance gave 0.3730 gram CO_2 and 0.1164 gram H_2O.

	Calculated for $C_{12}H_{18}O_6N_2$.	Found.
C	50.32	50.33
H	6.30	6.44
N	9.79	9.73

The calcium salt, made by prolonged digestion of an aqueous solution of the lactone with powdered calcium carbonate, is soluble in about three parts of hot water and twenty parts cold water, and separates out from hot concentrated solutions on standing in short glistening needles containing five molecules of crystal water; these may be driven off by heating to 100°, but with some decomposition.

0.3293 gram air-dry salt, from *d*-fructose, gave, on ignition, 0.0360 gram CaO.

	Calculated for $C_6H_{11}O_7Ca.5H_2O$.	Found.
Ca	7.69	7.80

The specific rotation of the anhydrous salt in 4 per cent. concentration was found to be —3°.06, *i. e.*, 1.2042 grams air-dry salt, corresponding to 0.9957 gram anhydrous salt, and 23.6803 grams water, therefore $p = 4.034$, $d = 1.011$, gave α in 2 dcm. tube = —0°.25. The specific rotation of another preparation from *d*-glucose was determined as —2°.9, *i. e.*, 1.2549 gram air-dry salt and 24.3177 grams water, therefore $p = 4.09$, $d = 1.011$, gave α in a 2 dcm. tube = —0°.24.

Constitution of the Acid—Conversion into d-*Trihydroxyglutaric Acid.*—It will be noticed that there is a remarkable resemblance in the properties of α-hydroxymethyl-*d*-arabonic acid and *d*-arabonic acid, as would be expected from their perfectly analogous structure. Arabonic lactone of the dextro series has a specific rotation of +73°.7 and melts at 96°; the phenylhydrazine melts at 215°, and the calcium salt crystallizes in needles with 5 molecules of crystal water;[1] the specific rotation of the calcium salt of *l*-arabonic acid has been found to be +3°.1.[2] Well-crystallized brucine, strychnine and quinine salts of *l*-arabonic acid have recently been described by Nef,[3] who also found that this acid could readily be separated from *d*-gluconic acid by means of the cinchonine salts.

[1] Ruff: Ber. d. chem. Ges., **32**, 550.
[2] Hauers and Tollens: *Ibid..* **36**, 3306.
[3] Ann. Chem. (Liebig), **357**, 226–7.

Since my α-hydroxymethyl-*d*-arabonic acid is very smoothly converted, by means of nitric acid, into a tribasic acid,

$$(COOH)_2 = COH \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} COOH,$$
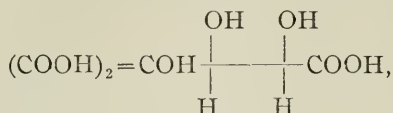
which by an asymmetric loss of carbon dioxide gives only *d*-trihydroxyglutaric acid, $COOH \overset{H}{\underset{OH}{|}} \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} COOH$, it is cer-

tain that the new hexonic acid just described must be either α-hydroxymethyl-*d*-arabonic acid,
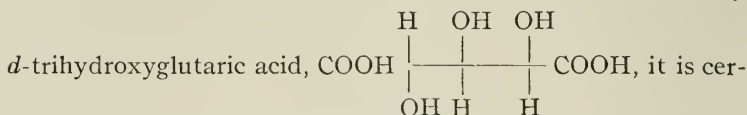
$$COOH \overset{HOH_2C}{\underset{OH}{|}} \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} CH_2OH, \text{ or } \alpha\text{-hydroxymethyl-}d\text{-rib-}$$
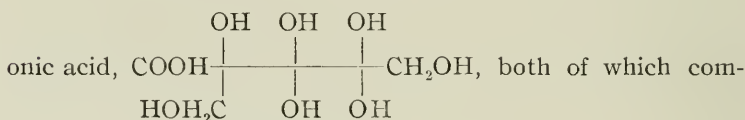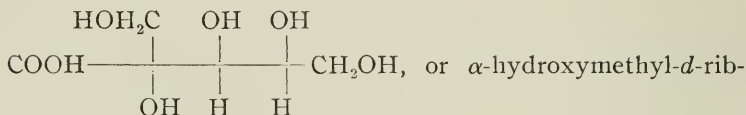
onic acid, $COOH \overset{OH}{\underset{HOH_2C}{|}} \overset{OH}{\underset{OH}{|}} \overset{OH}{\underset{OH}{|}} CH_2OH$, both of which com-

pounds can obviously give, by oxidation of the two primary alcohol groups present, one and the same tribasic acid,

$$(COOH)_2 = COH \overset{OH}{\underset{H}{|}} \overset{OH}{\underset{H}{|}} COOH;$$ this acid might, by loss
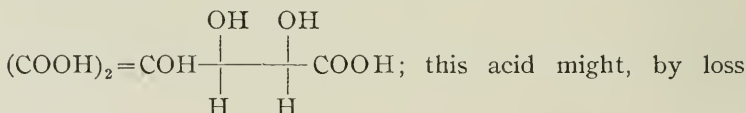
of carbon dioxide, give both ribo- as well as *d*-trihydroxy-glutaric acid, but remarkably enough it loses carbon dioxide asymmetrically and therefore gives only one of the two trihydroxyglutaric acids, namely, the optically active one. I consider the other possible formula for my new hexonic acid, namely, that of α-hydroxymethyl-*d*-ribonic acid, as ex-tremely improbable, since *d*-ribonic lactone gives, with alka-loids or bases, practically no crystalline derivatives other than the low melting phenylhydrazide and the cadmium salt.[1]

The formation of α-hydroxymethyl-*d*-arabonic acid from

[1] Fischer and Piloty: Ber. d. chem. Ges., **24**, 4216.

α- and β-*d*-glutose, as predicted by Nef,[1] obviously takes place by a transformation of the 2-3-osone,

$$CH_2OH - \overset{O}{\underset{\|}{C}} - \overset{O}{\underset{\|}{C}} \underset{\underset{H}{|}}{\overset{OH}{\overset{|}{}}} \underset{\underset{H}{|}}{\overset{OH}{\overset{|}{}}} CH_2OH,$$
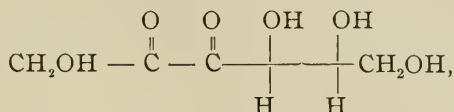
(which is common to both these sugars) by an *entire* asymmetric benzilic acid rearrangement; the constitution of the glutose sugars as 3-ketohexoses is thereby also definitely established.

Twenty-nine grams of air-dry calcium α-hydroxymethyl-*d*-arabonate treated with the calculated amount of oxalic acid gave, in the usual way, 18.52 grams of the crude lactone gum; this was heated[2] with 62.5 cc. of nitric acid (sp. gr. 1.2) for four days between 45° and 55°. The water and excess of nitric acid were then removed by several distillations under 15–25 mm. pressure in a bath kept at 50° (adding water after each operation, etc.). A very thick gum, 17.59 grams, remained, which consisted mainly of the above-mentioned
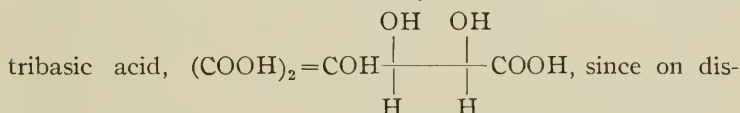
tribasic acid, $(COOH)_2 = COH \underset{\underset{H}{|}}{\overset{OH}{\overset{|}{}}} \underset{\underset{H}{|}}{\overset{OH}{\overset{|}{}}} COOH$, since on dis-

solving in 100 cc. water, and heating for seven hours under a reflux condenser in a bath kept between 120°–130°, streams of carbon dioxide were evolved. The aqueous solution was then digested with powdered calcium oxide in half-gram portions until no more calcium oxalate was deposited; the addition of lime to the aqueous filtrate was then continued until on long boiling the solution remained permanently alkaline. Carbon dioxide was then passed through the solution to get rid of the excess of calcium hydroxide, and a very careful examination of the rather difficultly soluble calcium salts obtained on concentrating the aqueous filtrate established with certainty the presence of only *d*-trihydroxyglutaric acid besides some unchanged α-hydroxymethyl-*d*-arabonate of calcium; not a trace of the isomeric ribotrihydroxyglutaric

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[1] Ann. Chem. (Liebig), **357**, 298.
[2] Kiliani: Ber. d. chem. Ges. **38**, 2671, 3624; **40**, 1238.

acid, which is optically inactive by intramolecular compensation, and the properties of which are well known,[1] could be found. The calcium salt of *d*-trihydroxyglutaric acid[2] separates out from the hot concentrated aqueous solutions as a gum; it is therefore best obtained in the crystalline form from moderately dilute solutions on scratching and standing; 6.98 grams of the salt were thus obtained in microscopic crystals, which, on recrystallization, gave 5.37 grams. A portion of this salt, 3.020 grams, dried four days over sulphuric acid *in vacuo*, lost 0.440 gram H_2O; and 0.3718 gram of the anhydrous salt gave, on ignition, 0.0933 gram CaO.

	Calculated for $C_5H_6O_7Ca.2H_2O$.	Found.
H_2O	14.26	14.56

	Calculated for $C_5H_6O_7Ca$.	Found.
Ca	18.34	17.92

The remainder of the salt was now converted, by means of oxalic acid, into the free acid; the crude product, 3.73 grams hard gum, on being dissolved in a small amount of acetone and adding dry ether, gave at first a gummy precipitate which was soon transformed by scratching into 2.05 grams of the white crystalline acid, $C_5H_8O_7$,[3] melting sharply at 175°. The specific rotation was found to be +28°.3; *i. e.*, 0.4075 gram and 8.1553 grams water (therefore $p = 4.75, d = 1.023$) gave $\alpha = +1°.38$ in a 1 dcm. tube.

That the gum left in the acetone-ether filtrate contained no ribotrihydroxyglutaric acid is certain from the following: It was first dissolved in water and freed from solvents, etc., by distillation under 25 mm. in a weighed flask which was heated finally on a boiling water bath. The gum, 1.48 grams, dissolved in 29.72 grams water ($p = 4.74$ and $d = $

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[1] Fischer and Piloty: Ber. d. chem. Ges., **24**, 4222.

[2] Boutroux: Compt. Rend., **127**, 1224. Lippmann: Ber. d. chem. Ges., **26**, 3060.

[3] Lippmann (*Loc. cit.*) first obtained this acid and gave the melting point 125° and $[\alpha]_D^{20} = +20°.8$. Ruff (Ber. d. chem. Ges., **32**, 550) then obtained the same substance from *d*-arabinose and gave the melting point 128° and $[\alpha]_D^{20} = +22°.8$. Recently Tollens and Rorive (Z. Ver. d. Zuckerind., **1909**, 579) have described the acid more fully; after repeated recrystallization they obtained a substance melting from 150°–160° (though not sharply) and giving $[\alpha]_D^{20} = +27°.6$.

1.013) gave $\alpha = +1°.45$ in a 1 dcm. tube, whence $[\alpha]_D^{20} = +30°.2$.

The crystalline acid obtained was further identified as *d*-trihydroxyglutaric acid by its conversion, by means of potassium carbonate, into the characteristic potassium salt.[1] The anhydrous salt was obtained in long transparent needles, giving a specific rotation of $-9°.5$; *i. e.*, 0.7895 gram and 19.5524 grams water (therefore $p = 3.88$ and $d = 1.017$) gave $\alpha = -0°.75$ in a 2 dcm. tube.

The aqueous filtrate from the 6.98 grams calcium *d*-trihydroxyglutarate mentioned above gave a further crop, 1.91 grams, of the same salt; from this 1.4 grams of the crude acid giving with acetone and ether only 0.5 gram of the crystallized acid, melting at 170°, were obtained. The latter showed a specific rotation of $+24°.15$, *i. e.*, 0.2229 gram and 6.6592 grams water (therefore $p = 3.23$, $d = 1.023$) gave $\alpha = +0°.80$ in a 1 dcm. tube. The noncrystalline gum still left in the solvent used gave a specific rotation of $+32°.5$; *i. e.*, 0.7 gram gum and 16.51 grams water (therefore $p = 4.06$ and $d = 1.023$) gave α in a 1 dcm. tube $= +1°.35$.

Finally the remaining noncrystalline lime salts left in the aqueous filtrate from the two crops of lime salts just mentioned yielded, on removing the calcium with oxalic acid, etc., a total of 1.97 grams acid gum, which gave a specific rotation of $+38°.8$; *i. e.*, 1.97 grams gum and 49.47 grams water (therefore $p = 3.82$) gave $\alpha = +1°.5$ in a 1 dcm. tube. It is therefore obvious that all the material obtained from the oxidation of α-hydroxymethyl-*d*-arabonic lactone after splitting off carbon dioxide, etc., was strongly dextrorotatory.

d-Galactose—α-Hydroxymethyl-d-*lyxonic Acid*,

$$\text{COOH}\overset{\displaystyle \text{HOH}_2\text{C} \quad\; \text{H} \;\; \text{OH}}{\underset{\displaystyle \text{OH} \;\;\; \text{OH H}}{\rule{3cm}{0.4pt}}}\text{CH}_2\text{OH}.$$—As already mentioned, 80.2
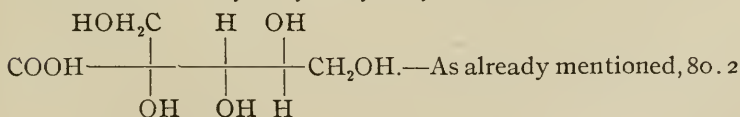
per cent. of *d*-galactose is converted by alkaline hydrogen peroxide into formic acid; a small amount, 4.65 per cent., of car-

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[1] Tollens and Rorive: *Loc. cit.* See also Will and Peters: Ber. d. chem. Ges., **22** 1698.

bon dioxide is also formed. The remaining fifteen per cent. of the sugar is converted into tar and into glycollic acid and a new hexonic acid which, by analogy and from its properties, is considered to be α-hydroxymethyl-*d*-lyxonic acid; it is formed from α- and β-*d*-galtose by oxidation to the common

$$2,3\text{-osone, } CH_2OH \overset{O}{\underset{}{C}} - \overset{O}{\underset{OH}{C}} \overset{H}{\underset{H}{\rule{0pt}{1em}}} \overset{OH}{\underset{}{\rule{0pt}{1em}}} CH_2OH, \text{ which then, by}$$
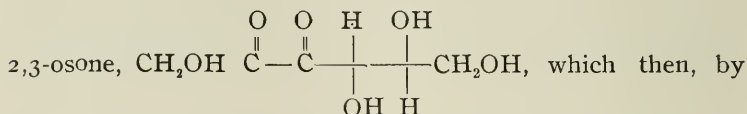
an entire asymmetric benzilic acid rearrangement, gives only one of the two isomeric acids theoretically possible.[1]

The nonvolatile gums obtained, after standing six days, etc., from the oxidation of 100 grams (in four portions) of *d*-galactose, melting at 167°–168°, with six molecules of hydrogen peroxide and nine molecules of sodium hydroxide weighed only 7.13 grams, as a decided amount of tar was formed. Threefold extraction of this gum with 300 cc. ether gave 4.43 grams of soluble and fairly mobile acid gum, which, by titration with 0.1 N alkali, was shown to consist of about 85 per cent. glycollic acid and 15 per cent. hexonic acid lactone. Glycollic acid was removed in great part from the mixture by means of the difficultly soluble strychnine salt, 10.88 grams of the pure salt, corresponding to 2.05 grams free acid, being actually obtained. The new hexonic acid was characterized by its brucine salt, crystalline plates melting from 171°–175° (1.9 grams obtained from alcohol), and especially by the quinine salt which crystallizes from hot water in long needles, is very difficultly soluble in this solvent in the cold, and melts at 213° (3.4 grams obtained). Finally the crude acid gum, obtained from either of these salts, gave very rapidly, on standing in the cold with 2 parts of 80 per cent. alcohol and 1 part of phenylhydrazine, a crystalline phenylhydrazide which became snow-white on washing with cold alcohol, melted sharply at 144°, and gave the following results on analysis:

0.1577 gram gave 13.4 cc. nitrogen at 21° and 745.7 mm. pressure.

[1] Nef: Ann. Chem (Liebig), **357**, 298.

0.1122 gram gave 0.0789 gram H_2O and 0.2081 gram CO_2.

	Calculated for $C_{12}H_{18}O_6N_2$.	Found.
C	50.32	50.49
H	6.30	7.87
N	9.79	9.50

From a comparison of the properties of the derivatives of my new hexonic acid with those of *d*-lyxonic and *l*-xylonic acids, as well as by analogy from my experiments with the members of the *d*-glucose series, I have come to the conclusion that *α*-hydroxymethyl-*d*-lyxonic acid must be present. Accordingly the new acid must be converted by oxidation with nitric acid into a tribasic acid,

$$(COOH)_2C(OH) \underset{\underset{\textstyle OH \quad H}{|\qquad\qquad|}}{\overset{\overset{\textstyle H \quad OH}{|\qquad\qquad|}}{\rule{3cm}{0.4pt}}} CH_2OH,$$
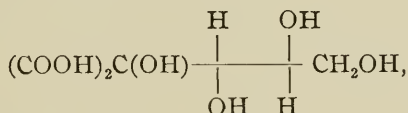
which, by loss of carbon dioxide, must give either *d*-trihydroxyglutaric or xylotrihydroxyglutaric acid. It is therefore my intention to carry out this oxidation experiment on a large scale in the near future. Moreover, instead of using *d*-galactose for the preparation of *α*-hydroxymethyl-*d*-lyxonic acid, I intend to start with *α*- and *β*-*d*-galtose, from which I expect to obtain this acid in splendid yield.

Glycol, Glycollic Acid and Formic Acid in the Presence of Alkaline Hydrogen Peroxide.

The following experiments show that ethyleneglycol, as well as glycollic acid, are very slowly oxidized by alkaline hydrogen peroxide, and give small amounts of formic and carbonic acids but no trace of oxalic acid. Formic acid, on the other hand, is not perceptibly oxidized. Since no trace of any other hydroxy acid, such as glycerinic, trihydroxybutyric acid, *d*-mannonic or *d*-gluconic acid was ever observed in my oxidation experiments with *d*-glucose and *d*-fructose, I have not as yet proved that these acids are also only slightly effected by alkaline hydrogen peroxide, but it is my intention to carry out such experiments soon.

(a) Two grams of ethyleneglycol, boiling at 193°, dissolved in 120 cc. of three per cent. hydrogen peroxide (three molecules), were added to a normal solution containing 7.24 grams (four molecules) of potassium hydroxide. The mixture stood for four days at room temperature; on working up as usual 0.13 gram formic acid, 1.25 grams unchanged glycol, and no trace of oxalic acid were obtained.

(b) Glycollic acid, two grams, was dissolved in 73 cc. three per cent. hydrogen peroxide (2.5 molecules) and added to a normal solution containing 4.48 grams (3 molecules) of potassium hydroxide. On working up after standing four days, 0.133 gram carbon dioxide and 0.125 gram of formic acid, besides 1.36 grams unchanged acid, were found. This shows that glyoxylic acid, which must first be formed by oxidation, gives equal molecular proportions of formic and carbonic acids, but no oxalic acid on further oxidation.[1]

(c) On allowing a mixture of 67 cc. three per cent. hydrogen peroxide (1.5 molecules), 1.71 grams formic acid, and 4.48 grams potassium hydroxide (2 molecules) in normal solution to stand for 3 days at ordinary temperature only a minute amount, not over 0.01 gram, of carbon dioxide was formed.

Part II.   On the Behavior of Hydrogen Peroxide towards Hexoses in the Presence of Traces of Iron Salts.

In 1894 Fenton[2] observed that tartaric acid dissolved in three per cent. hydrogen peroxide is rapidly oxidized if a trace of ferrous sulphate be added; similar observations were also made by him in the case of many hydroxy acids as well as polyatomic alcohols. Cross, Bevan and Smith,[3] as well as Morrell and Crofts,[4] have applied Fenton's reaction to the carbohydrates and have determined the character of some of the oxidation products found. By the use of hydrogen peroxide and small amounts of ferric acetate Ruff[5] was also able to convert the hexonic and pentonic acids, with loss of carbon dioxide, into pentose and tetrose sugars.

[1] Cf. Denis: This Journal, **38**, 361.
[2] J. Chem. Soc., **65**, 899; **75**, 1; **77**, 69, 1294.
[3] *Ibid.*, **73**, 463.
[4] *Ibid.*, **75**, 786; **77**, 1219; **81**, 666; **83**, 1284; **87**, 280.
[5] Ber. d. chem. Ges., **31**, 1573; **32**, 550, 3672; **33**, 1798; **34**, 1362.

Fenton supposed that the ferrous salt had a specific effect in the reactions under consideration, whereas Ruff attributes the catalytic effect to the presence of the ferric salt; my own observations show that the reactions go equally well in the presence of traces of a ferric or ferrous salt. It was found that whether a ferrous or ferric salt be used, the iron in solution in hydrogen peroxide is always in the ferrous condition as long as there is simultaneously present a reduceable substance (*e. g.*, sugar, etc.); as soon as the latter is consumed the iron is oxidized to the ferric condition. It is evident from Nef's work[1] on alcohols and their salts that the addition of the iron salt serves simply to give, through intermediate salt formation, an increase in the percentage of existing methylene dissociation. The conversion by Ruff of calcium *d*-gluconate into *d*-arabinose, etc., therefore simply proves that the iron salt,

$$
\text{COOca} \overset{\text{Ofe}\quad\text{H}\quad\ \text{OH}\quad\text{OH}}{\underset{\text{H}\quad\ \ \text{OH}\quad\text{H}\quad\ \ \text{H}}{\rule{0pt}{1pt}\text{———}\rule{0pt}{1pt}}}\text{—CH}_2\text{OH} \rightleftarrows
$$

$$
\text{feOH} + \text{COOca} \overset{\text{H}\quad\ \text{OH}\quad\text{OH}}{\underset{\text{OH}\quad\text{H}\quad\ \ \text{H}}{\rule{0pt}{1pt}\big|\text{———}\big|}}\text{—CH}_2\text{OH},
$$
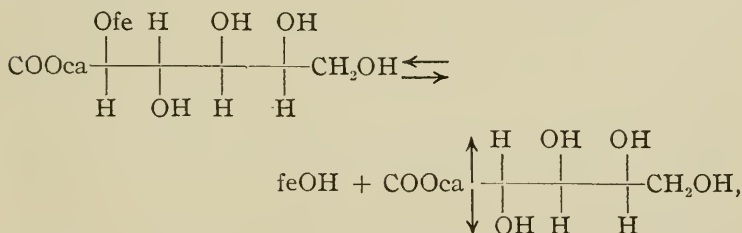
is mainly formed, which then, in the dissociated condition, oxidizes to the α-keto acid with subsequent spontaneous loss of carbon dioxide, and formation of *d*-arabinose, etc. Obviously only a trace of iron salt is necessary, just as in the conversion of alcohol into ether by sulphuric acid. Since, moreover, Ruff[2] also proved that a small amount of 4-keto-gluconic acid is formed in the reaction we must conclude that
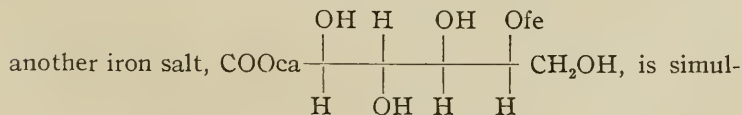
another iron salt, $\text{COOca} \overset{\text{OH}\quad\text{H}\quad\ \ \text{OH}\quad\text{Ofe}}{\underset{\text{H}\quad\ \ \text{OH}\quad\text{H}\quad\ \ \text{H}}{\rule{0pt}{1pt}\text{———}\rule{0pt}{1pt}}}\text{CH}_2\text{OH},$ is simul-

taneously present; from a theoretical standpoint there

[1] Ann. Chem. (Liebig), **318**, 138; **335**, 312; **357**, 294–312.
[2] Ber. d. chem. Ges., **32**, 2269.

is the possibility of formation of five different iron salts with calcium *d*-gluconate.[1] The fact observed by Morrell that *d*-fructose and *d*-glucose give with one molecule of hydrogen peroxide and traces of iron salts a fair amount of 1,2-glucosone therefore simply proves that the iron salts formed by these sugars possess the constitution

$$CH_2OfeC \underset{\substack{| \\ OH}}{\overset{\substack{O \quad H \\ || \quad |}}{—}} \underset{\substack{| \\ H}}{\overset{\substack{OH \\ |}}{—}} \underset{\substack{| \\ H}}{\overset{\substack{OH \\ |}}{—}} CH_2OH \text{ and}$$

$$O{=}CH \underset{\substack{| \\ H}}{\overset{\substack{Ofe \\ |}}{—}} \underset{\substack{| \\ OH}}{\overset{\substack{H \\ |}}{—}} \underset{\substack{| \\ H}}{\overset{\substack{OH \\ |}}{—}} \underset{\substack{| \\ H}}{\overset{\substack{OH \\ |}}{—}} CH_2OH, \text{ etc.}$$
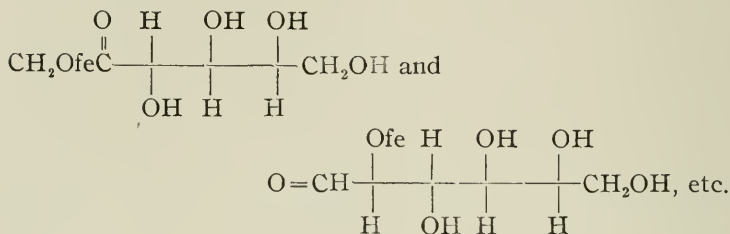
I therefore began a further study of the action of hydrogen peroxide towards various sugars in the presence of small amounts of ferrous or ferric sulphate from this standpoint. Morrell and Crofts used from one to four molecules of hydrogen peroxide in their experiments with *d*-glucose, *d*-fructose and *d*-galactose, and isolated, besides the 1,2-hexosone, glycollic, glyoxylic and oxalic acids as definite oxidation products. They state also that erythronic acid (trihydroxybutyric acid) is formed from *d*-glucose and *d*-fructose, especially when 4 molecules of hydrogen peroxide were used. The various isomeric trihydroxybutyric acids are now known to give very striking and easily identified derivatives.[2] I tried, by repeating Morrell's experiment, to determine which of these acids were actually present, but never found any of them. I am therefore of the opinion that a keto acid or a mixture of keto acids containing four carbon atoms was actually present instead of erythronic acid, but I was unable to prove this by the isolation of crystalline derivatives. It is obvious that 1,2-glucosone, the common oxidation product of dextrose and laevulose, might easily give by further salt formation, subsequent oxidation, etc., a 1,2,3-osone,

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[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 255, 283.
[2] Ruff: Ber. d. chem. Ges., **32**, 3674: **34**, 1362. Nef: Ann. Chem. (Liebig), **357**, 247. Anderson: THIS JOURNAL, **42**, 423.

$$O = CH - C = O - C = O \underset{H}{\overset{OH}{\mid}} \underset{H}{\overset{OH}{\mid}} CH_2OH; \quad a \quad 1,2,3,4\text{-osone},$$

$$CHO - C = O - C = O - C = O - C \underset{H}{\overset{OH}{\mid}} CH_2OH; \quad \text{etc.,} \quad \text{and}$$
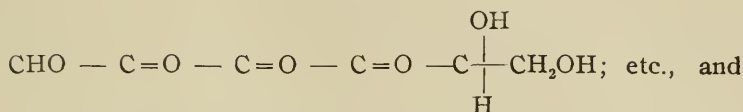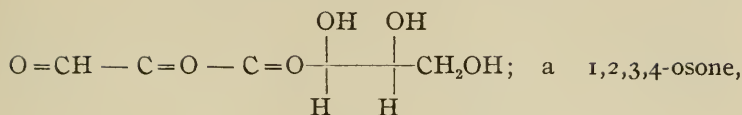
the decisive results which I have obtained with *d*-galactose, *d*-glucose and *d*-fructose by using an excess (14 molecules) of hydrogen peroxide in the presence of ferrous or ferric sulphate can only be explained on the assumption that intermediate products of this character are first formed. The three sugars named burn under these conditions completely to give varying amounts of formic, carbonic and oxalic acids; my experiments prove also that the formic acid first formed is readily further oxidized to carbon dioxide by hydrogen peroxide and iron salts, whereas oxalic acid remains practically unaltered in the presence of these reagents, Now glycol, glycerol and their oxidation products, diose and triose, never give more than minimal traces of, if any, oxalic acid when treated with hydrogen peroxide and iron salts; they burn exclusively to formic and carbonic acids. I consider therefore that the formation of large amounts of oxalic acid, from 18 to 27 per cent., from the hexoses named, must be due to a direct hydrolysis of such polyhexosones first formed from the hexoses by oxidation.

On the Quantitative Oxidation of Hexoses with an Excess of Hydrogen Peroxide (14 Molecules) in the Presence of Iron Salts.

The sugar to be oxidized was dissolved in water, mixed with an aqueous solution containing 0.25 to 0.75 of a molecule of ferrous or ferric sulphate, and an excess (14 molecules) of three per cent. hydrogen peroxide was then slowly added through a separatory funnel. The oxidation took place with some evolution of heat at first, but the mixture was allowed to stand for 20 hours at ordinary temperature in the regular apparatus used for the determination of carbon dioxide men-

tioned under Part I. All the carbon dioxide formed in the oxidation was collected as usual in the barium hydroxide cylinders. After removing the sulphate present by addition of the calculated amount of barium hydroxide, etc., the free formic acid present in the aqueous solution was removed by distillation at reduced pressure as described under Part I. The iron present in the water solution of the nonvolatile residue was then precipitated by ammonium sulphide and the filtrate, freed from hydrogen sulphide by boiling, then gave with ammonia and calcium chloride a precipitate of calcium oxalate, which was purified by dissolving in dilute hydrochloric acid, reprecipitating with ammonia, adding acetic acid, filtering and weighing, after drying at 100°, as the salt $C_2O_4Ca.o.5H_2O$.

On adding slowly 190 cc. of a 2.84 per cent. solution of hydrogen peroxide to an aqueous solution of 2 grams d-galactose and 2.04 grams ferric sulphate, $Fe_2(SO_4)_3.5H_2O$, in 40 cc. water, a noticeable evolution of heat took place within the first hour, which was controlled by keeping the mixture in a bath at 20°. Entirely similar experiments were carried out with 2 grams d-fructose and 2 grams d-glucose with the following results after standing 20 hours at room temperature:

	Carbon dioxide.		Formic acid.		Oxalic acid.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
d-Galactose,	2.03	69.28	0.092	3.0	1.13	26.9
d-Glucose,	2.08	70.98	0.092	3.0	0.70	16.66
d-Fructose	2.13	72.69	0.024	0.77	0.76	18.89

A quantitative experiment with 2.87 grams *formic acid* and 3.7 grams ferric sulphate (0.25 molecule) in 80 cc. water showed that the oxidation took place at once on adding 69 cc. of a 2.87 per cent. solution of hydrogen peroxide; after standing seven hours 2.14 grams of carbon dioxide, 78.1 per cent., had been formed and only 0.32 gram of free formic acid was recovered; the solution contained ferric formate.

A similar experiment with 2 grams crystallized *oxalic acid* and 0.97 gram ferric sulphate (0.25 molecule) in 70 cc. water, gave, after adding 24 cc. of a 2.3 per cent. solution of hydrogen

peroxide and standing six hours only, 0.04 gram carbon dioxide, *i. e.*, 3.1 per cent., besides 1.91 grams unchanged oxalic acid.

When *glycollic acid*, 2 grams, and ferric sulphate, 1.63 grams (0.25 molecule), were dissolved in 45 cc. water and treated with 90 cc. of a 2.95 per cent. solution of hydrogen peroxide (3 molecules), the amount of carbon dioxide found, after standing 20 hours, was 1.96 grams, or 84.84 per cent.; in addition 0.396 gram formic acid, 10.75 per cent., but no trace of oxalic acid, could be found.

Two grams of *ethyleneglycol*, which has been proved by Fenton[1] to give glycollic aldehyde (diose) as an intermediate product, gave, when treated in aqueous solution with 1.75 grams ferric sulphate and 228 cc. of a 2.9 per cent. solution of hydrogen peroxide (6 molecules), after standing 96 hours, 2.54 grams carbon dioxide, 89.78 per cent., besides 0.24 gram formic acid, but no trace of oxalic acid.

Finally two grams of glycerol (which had been shown by Fenton to give first glycerinic aldehyde), 1.3 grams ferric sulphate (0.25 molecule), and 210 cc. of a 2.44 per cent. solution of hydrogen peroxide (7 molecules) gave, after standing 24 hours, 1.99 grams carbon dioxide (67.79 per cent.), 0.74 gram formic acid, 24.77 per cent., and just a trace, less than 0.001 gram, of oxalic acid.

Finally, I give here a brief summary of some quantitative experiments carried out with *d*-galactose and *d*-fructose with from 1 to 4 molecules of hydrogen peroxide in the presence of small amounts of iron salts. It will be seen that even under these conditions much formic and carbonic acids are formed, a fact which has been overlooked by Morrell in his work; oxalic acid, on the other hand, was present only in small amounts.

d-Galactose and Four Atoms Oxygen.—Twenty-five grams *d*-galactose, 60 cc. water, 0.2 gram iron vitriol, $FeSO_4.7H_2O$, and 646 cc. of a 2.9 per cent. solution of hydrogen peroxide gave, after standing 14 hours, 5.05 grams carbon dioxide and 6.5 grams formic acid. Treatment of the nonvolatile gum,

[1] J. Chem. Soc., **75**, 1.

17 grams, with an excess of powdered calcium carbonate, etc., gave only 0.85 gram calcium oxalate, corresponding to 0.59 gram crystallized oxalic acid, and addition of alcohol to the concentrated aqueous filtrate (after decolorizing with charcoal, etc.), gave 15.05 grams precipitated calcium salts containing 12.07 per cent. calcium and reducing Fehling's solution; only 1.51 grams dark neutral gum was found in the aqueous alcoholic filtrate. On precipitating the calcium in the soluble salts with the calculated amount of oxalic acid, etc., I was able to prove the presence of a small amount of glycollic acid by the isolation of the characteristic strychnine salt (6.0 grams, corresponding to 1.1 grams acid), but obtained no other definite products by means of brucine or phenylhydrazine.

In another experiment in which 10 grams of *d*-galactose, 0.1 gram of iron vitriol, 20 cc. of water and 202 cc. of 1 per cent. hydrogen peroxide (1 molecule) were used, the amount of formic acid obtained, after standing 24 hours, was 0.33 gram; a large amount of neutral nonvolatile gum was also obtained, but this could not be handled. A similar experiment with 2 molecules of the oxidizing agent gave 0.44 gram carbon dioxide and 0.644 gram of formic acid from 10 grams of *d*-galactose.

d-*Fructose and Four Atoms Oxygen.*—A mixture of 25 grams of laevulose, 0.65 gram iron vitriol, 100 cc. of water and 648 cc. of a 2.89 per cent. solution of hydrogen peroxide gave, after standing five days, precipitating the sulphuric acid by means of barium hydroxide, etc., 22 grams of dark brown gum; this was converted by heating for 8 hours with 66 cc. of acetic anhydride, etc., into 28.1 grams of acylated gum (after heating to 100° under 20 mm. pressure) of which, on threefold thorough digestion with 500 cc. of ether each time, only 7.08 grams dissolved, leaving 21.8 grams of granular, insoluble, dark brown tar. The ether-soluble acylated gums were proved to contain glycollic acid on hydrolysis with water.

CAMPHOR.[1]

By G. Blanc.

The formula now assigned to camphor and which may be written, as is most convenient, in either of the three forms,

$$C_8H_{14} \Big\langle \begin{matrix} CO \\ | \\ CH_2 \end{matrix} \Big. ,$$

$$\begin{matrix} CH_3 \\ | \\ C \\ CH_2 \diagup \quad | \quad \diagdown CO \\ \quad | \; CH_3.C.CH_3 \; | \\ CH_2 \diagdown \quad | \quad \diagup CH_2 \\ CH \end{matrix} ,$$

or

$$\begin{matrix} CH_3 \;\; CH_3 \\ \diagdown C \diagup \\ CH \diagup \quad \diagdown C.CH_3 \\ | \quad CH_2-CO \quad | \\ CH_2 \underline{\qquad\qquad} CH_2 \end{matrix} ,$$
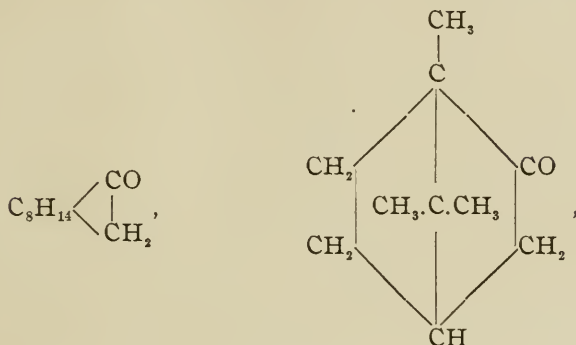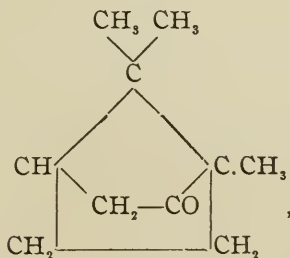
appear to follow quite naturally from the known properties of camphor and it does not seem as if its derivation should have caused any particular difficulty. But such a supposition is quite erroneous for, as a matter of fact, before the truth was definitely established an enormous amount of work had to be done and several constitutional formulas which, as the problem was developed, appeared successively to be more probably the correct ones had to be considered. This considerable difficulty in the working out of a problem which, now that it is solved, seems quite simple, was due to several

causes, the two principal ones of which were, beyond doubt, the then very incomplete knowledge possessed by chemists, and which is still very limited, as to the behavior of hetero-cyclic chains, and especially the ease with which the camphor molecule and its direct decomposition products undergo transformations.

To these unfortunate transformations, which were then unsuspected, were due the bitter polemics that for several years divided chemists, perfectly well-established experimental facts leading to radically false theoretical deductions.

In this address I will attempt to demonstrate the subtlety of the later researches which finally led to the establishment of the truth, and to bring out the part taken by each investigator in this work. I wish at the outset to beg indulgence for having to enter into personalities and to mention some of my colleagues only to say that they were in error.

Moreover, the same thing has happened to me and, indeed, it can be said that no one who took an active part in the controversy escaped a similar misadventure.

I will begin with a very brief résumé of the whole question, and in order not to go too far back I will take up the first formula which really deserves any attention.

Kekulé's formula,[1]

$$\begin{array}{c} CH_3 \\ | \\ C \\ \end{array}$$

CH⟨ ⟩CO
CH₂⟨ ⟩CH₂
CH
|
CH
CH₃ CH₃
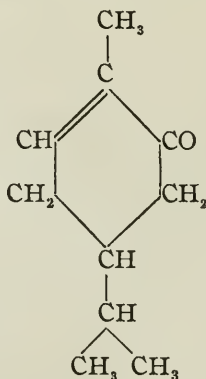
took into account, at the time when it was proposed, certain very important facts which could serve as the basis for es-

[1] See Wurtz's dictionary, second suppl., p. 931.

tablishing a constitutional formula, *viz.*, the transformation of camphor into *p*-cymene by the action of phosphoric anhydride, and into carvacrol by means of iodine. But it was not long before it was seen that the camphor molecule probably contains no double bond, for no stable addition product is known. On the basis of this observation, several formulas were proposed in which it was attempted to account for the two missing hydrogen atoms by the presence of a bond between two nonadjacent carbon atoms, *e. g.*,

$$CH_3$$
$$|$$
$$C$$

$$CH_2 \diagup \qquad \diagdown CO$$
$$CH_2 \diagdown \qquad \diagup CH_2$$

$$C$$
$$|$$
$$CH$$
$$\diagup \diagdown$$
$$CH_3 \quad CH_3$$
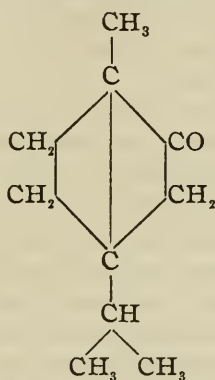
Bredt's first formula.

Certain stereochemical considerations led Bouveault to propose a formula in which the extra bond was placed somewhat differently, *viz.*, the carbon atom to which was attached the methyl group was united, not to the opposite para carbon atom, but to a carbon of the isopropyl group:

$$CH_3$$
$$|$$
$$C$$

$$CH_2 \diagup \qquad \diagdown CO$$
$$\qquad CH_2$$
$$CH_2 \diagdown \quad CH.CH_3 \quad CH_2$$

$$CH$$
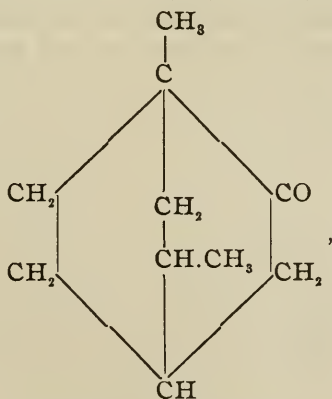
Bouveault's first formula.

As we shall see later, this idea was not a fortunate one, for a second solution presented itself, *viz.*, union with the tertiary carbon of the isopropyl group; it is extremely regrettable that Bouveault, ill inspired, did not think of it, for this proved to be the correct solution. But, to be sure, he could not guess this.

Nevertheless, the problem was by no means definitely solved, and the new facts observed in different directions, especially in connection with camphoric acid, did not seem to advance its solution (in fact, just the contrary) or to crystallize opinions as to the relative merits of the Kekulé formula and its modifications.

It seemed, in fact, that camphoric acid, thanks to its singular properties, offered a new and interesting field for investigation and that the solution of the problem was to be sought through this compound.

Camphor results from the union of two pentagonal rings to form a third hexagonal one and we know that the derivation of a formula for such a substance cannot be effected easily. Logically, the problem must be simplified by studying a product derived directly from camphor and containing but one ring.

We shall see that camphoric acid alone could furnish the desired result.

In fact, we have three principal methods available for effecting the desired change in the camphor molecule, *i. e.*, the breaking open of one chain, leaving a monocyclic compound.

(1) The addition of the elements of water by means of alkalis, under proper conditions, with the formation of campholic acid:

$$\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
\diagup \quad \diagdown \\
CH_3 \cdot CH \qquad\qquad C\diagup^{CH_3}_{CO_2H} \\
| \qquad\qquad\qquad | \\
CH_2\text{———}CH_2
\end{array}$$
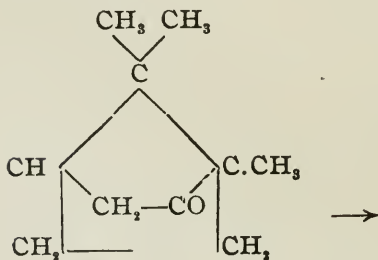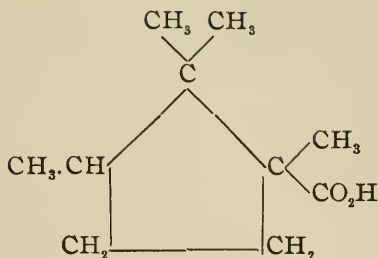
Now that we know the correct formula for campholic acid, it is not difficult to see why the investigations undertaken to determine its constitution, especially that of Guerbet,[1] were doomed to failure. This acid contains a carboxyl group attached to a tertiary carbon atom and the analytical methods usually employed (bromination, then removal of hydrobromic acid and oxidation) cannot be used.

The study of the unsaturated hydrocarbon campholene, derived from this acid by the loss of $CO + H_2O$, might lead to interesting conclusions, but campholene is itself already a transformation product:

$$\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
\diagup \quad \diagdown \\
CH_3 \cdot CH \qquad C\diagup^{CH_3}_{CO_2H} \\
| \qquad\qquad | \\
CH_2\text{——}CH_2
\end{array}
\longrightarrow
\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
\diagup \quad \diagdown \\
CH_2 \qquad C \cdot CH_3 \\
| \qquad\qquad \| \\
CH_2\text{——}C \cdot CH_3
\end{array};$$
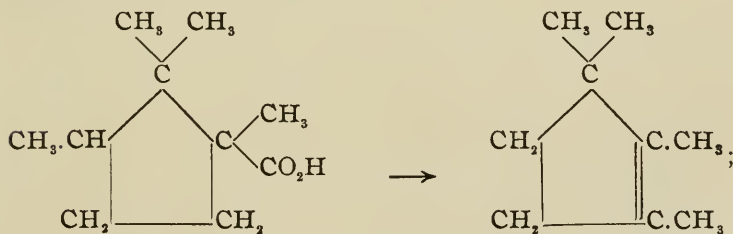
and, moreover, the methods employed by Guerbet (heating with fuming hydriodic acid) bring about other and still more deep-seated changes.

Misled by these numerous and unsuspected transformations, Guerbet could not, therefore, draw correct conclusions.

(2) The opening of one ring (the same as in the case of the campholic acid, although in a slightly different manner),

[1] Thesis, Paris, 1894.

starting from camphoroxime. The normal reaction is repre-
sented as follows:

$$
\begin{array}{c}
CH_3 \ CH_3 \\
\diagdown / \\
C \\
/ \qquad \diagdown \\
CH \diagup \qquad C.CH_3 \\
CH_2 \!-\!-\!-\!-\! C \\
\qquad \| \\
\qquad HON \\
CH_2 \!-\!-\!-\!-\!-\! CH_2
\end{array}
\qquad \longrightarrow
$$

$$
\begin{array}{c}
CH_3 \ CH_3 \\
\diagdown / \\
C \\
/ \qquad \diagdown \\
CN.CH_2.CH \diagup \qquad C.CH_3. \\
CH_2 \!-\!-\!-\!-\! CH
\end{array}
$$
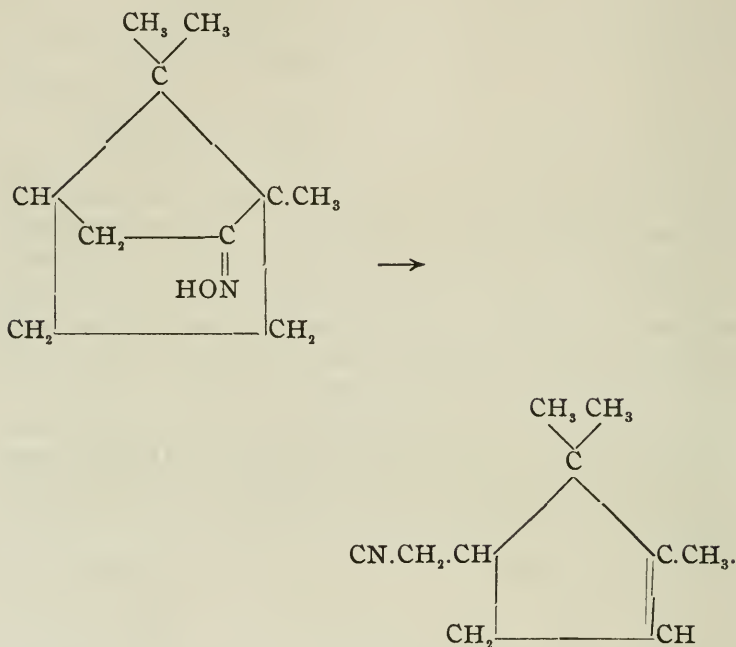
The product so obtained (α-campholenonitrile) can, with-
out difficulty, be converted into the acid, which lends itself
more easily to investigation than campholic acid.

Unfortunately, such investigation is extraordinarily diffi-
cult, and the chemists (Béhal,[1] Tiemann[2]) who have devoted
themselves to it have been able to obtain only incomplete
results which, though very interesting, to be sure, are not de-
cisive. For, as a matter of fact, the conversion of camphor-
oxime into α-campholenonitrile is always accompanied by
the formation in greater or less quantity, by a process which
I shall explain later in connection with the α- and β-cam-

[1] Compt. Rend., **120**; Bull. Soc. Chim., [3] **13**, 844.
[2] Dict. Chim. Gén., **28**, 2166; **29**, 3806; **30**, 242, 321, 404.
Ber. d. chem. ges.

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pholytic acids, of a transformation product, β-campholeno-
nitrile:

$$CN.CH_2.CH \underset{CH_2}{\overset{CH_3\ CH_3}{C}} C.CH_3 \quad CH \longrightarrow$$

$$CH_2 \underset{CH_2}{\overset{CH_3\ CH_3}{C}} C.CH_3 \quad C.CH_2CN$$

Then, too, the study of the two resulting acids (α- and
β-campholenic acids) bristles with difficulties, owing to nu-
merous molecular transformations.

(3) There remains, then, camphoric acid, whose relation
to camphor is well known. It is derived from the latter by
oxidation with nitric acid:

$$C_8H_{14} \begin{cases} CH_2 \\ | \\ CO \end{cases} \longrightarrow C_8H_{14} \begin{cases} CO_2H \\ CO_2H \end{cases} .$$

We must not assume that the formula is the evidence itself,
or that it was at once accepted by every one.

Indeed, camphoric acid would seem, from this formula,
to be a dicarboxylic acid. Now, the properties of the two
acid groups are so different that Friedel[1] assumed that the
extreme feebleness of one of them was due to its being, not a
carboxyl group, but an acid hydrogen between two electro-
negative groups. Kekulé's formula lends itself well to such
an assumption:

[1] Wurtz's Dict., second suppl., p. 931; and Compt. Rend., **113**, 825.

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{C} \\
\end{array}
\qquad
\begin{array}{c}
\text{CO}_2\text{H} \\
| \\
\text{C.OH} \\
\end{array}
$$

At first sight, such a formula seemed very alluring, but the facts which daily accumulated soon overthrew it.

First, it was shown directly that camphoric acid really does contain two carboxyl groups.

This was demonstrated simultaneously in several ways; I will cite only one very decisive proof.

Camphoric acid is extremely asymmetric, the two acid groups having entirely different properties; thus, a mon-amide corresponding to each of them (α- and β-camphoramic acids) is known.

Each of these α- and β-camphoramic acids, when treated with bromine and sodium hydroxide (Hofmann's reaction), is converted into an amino acid by the loss of carbon monoxide.[1] Each of the amide groups consists, therefore, of the CO.NH₂ grouping.

We admit, then, that the relation between camphor and camphoric acid,

$$
\text{C}_8\text{H}_{14}\Big\langle
\begin{array}{c}
\text{CH}_2 \\
| \\
\text{CO}
\end{array}
\qquad \longrightarrow \qquad
\text{C}_8\text{H}_{14}\Big\langle
\begin{array}{c}
\text{CO}_2\text{H} \\
\text{CO}_2\text{H}
\end{array},
$$

is sufficiently proved.

This reaction yields, of course, but one acid, since both the

[1] Noyes: This Journal, **16**, 317, 500; **17**, 421; Diet. Chim. Gen., **28**, 547; This Journal, **18**, 686; Diet. Chim. Gen., **29**, 2326.   *Ber. d. chem. Ges.*

Ben d. chem. ʒes.

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CH_2 and CO groups of the complex —$CH_2.CO$— are converted into carboxyl groups.

But, furthermore, to the clean-cut conversion of camphor into camphoric acid corresponds the no less well-defined conversion of this acid into camphor.

Haller[1] has shown that camphoric anhydride is converted, by reduction with sodium amalgam, into a lactone, campholide:

$$C_8H_{14}{<}^{CO}_{CO}{>}O \qquad \longrightarrow \qquad C_8H_{14}{<}^{CH_2}_{CO}{>}O.$$

This campholide, when treated with potassium cyanide, goes over into the nitrile of an acid which Haller called homocamphoric acid:

$$C_8H_{14}{<}^{CH_2}_{CO}{>}O + CNK = C_8H_{14}{<}^{CH_2.CN}_{CO_2K} \longrightarrow$$

$$C_8H_{14}{<}^{CH_2.CO_2H}_{CO_2H}.$$
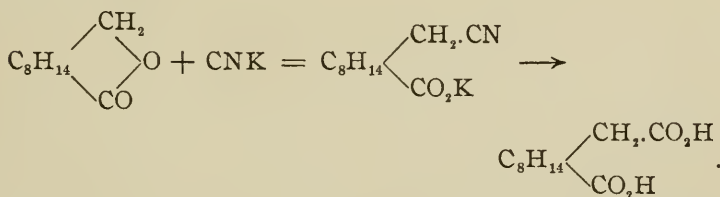
Finally, this homocamphoric acid can be converted into the lead salt which, when heated, yields camphor:

$$C_8H_{14}{<}^{CH_2.CO_2H}_{CO_2H} \qquad \longrightarrow \qquad C_8H_{14}{<}^{CH_2}_{CO}.$$

The whole question now resolved itself into the determination of the constitution of camphoric acid. This problem has been the subject of considerable investigation, and it was only after several years of earnest work that it was solved.

In order to discuss it at its most interesting stage, we shall take up the question as it stood towards the end of the year 1897.

At that time two formulas were under consideration, Tiemann's and Bredt's second formula:

[1] Compt. Rend., **122**, 293, 446.

$$\text{CH}_3 \quad \text{CH}_3$$
$$\diagdown \diagup$$
$$\text{C}$$

$$\text{CO}_2\text{H.CH} \diagup \qquad \diagdown \text{CH.CH}_3$$
$$\text{CH}_2 \rule{1cm}{0.4pt} \text{CH.CO}_2\text{H}$$

Tiemann's formula.

$$\text{CH}_3 \quad \text{CH}_3$$
$$\diagdown \diagup$$
$$\text{C}$$

$$\text{CO}_2\text{H.CH} \diagup \qquad \text{C} \diagup^{\text{CH}_3}_{\diagdown \text{CO}_2\text{H}} \cdot$$
$$\text{CH}_2 \rule{1cm}{0.4pt} \text{CH}_2$$
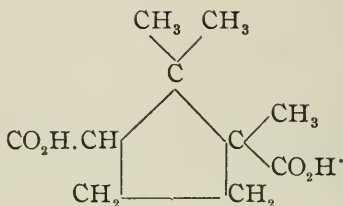
Bredt's formula.

Let us see how these formulas were derived.

Tiemann's formula[1] is derived from that which he assigned to camphor from its relation to pinene. This point being quite complex and beyond the scope of the subject which I propose to consider, I shall not discuss it. I shall merely state that it was very soon found that this formula was not in harmony with certain very interesting facts, especially the formation, from camphoric acid, by oxidation, of camphoronic acid whose synthesis had just been effected by Perkin, Jr., and J. F. Thorpe.[2]

In act, the compound

$$\text{CH}_3 \quad \text{CH}_3$$
$$\diagdown \diagup$$
$$\text{C}$$

$$\text{CO}_2\text{H.CH} \diagup \qquad \diagdown \text{CH.CH}_3$$
$$\text{CH}_2 \rule{1cm}{0.4pt} \text{CH.CO}_2\text{H}$$
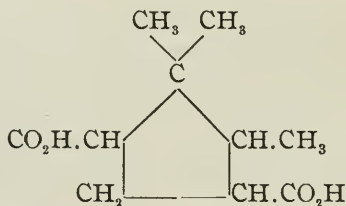
cannot give

[1] Dict. Chim. Gén., **28**, 1079.
[2] J. Chem. Soc., **91**, 1169.

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
\diagup \quad \diagdown \\
CO_2H \diagup \qquad C \diagup CH_3 \\
\diagdown CO_2H \\
CO_2H \text{———} CH_2
\end{array}
$$
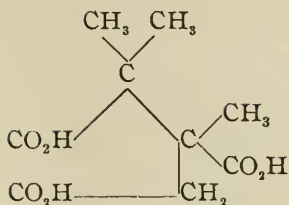
There remains, then, Bredt's formula.

As you will remember, we saw how Bouveault modified Kekulé's camphor formula by changing the double bond, the existence of which was very doubtful, into a cross bond, properly placed.

A short time after the publication of Bouveault's paper, Koenigs announced that when camphoric acid is oxidized with potassium permanganate, dimethylmalonic acid,

$$
\begin{array}{c}
CH_3 \qquad CH_3 \\
\diagdown \quad \diagup \\
C \\
\diagup \quad \diagdown \\
CO_2H \qquad CO_2H
\end{array} \text{,}
$$
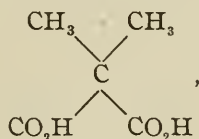
is obtained. Camphoric acid and, consequently, camphor must then contain the grouping $C\diagup{\diagdown}{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}$; this extremely important observation led Bredt to modify Bouveault's formula by making the union through the tertiary carbon atom of the isopropyl group:

CH_3
|
C
...

Kekulé's formula.

Bouveault's formula.
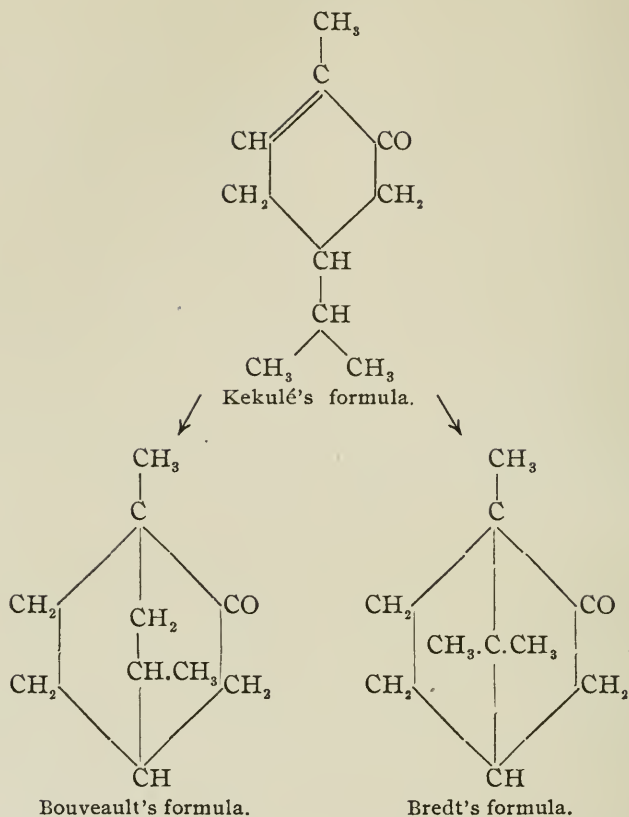
Bredt's formula.

Such is the origin of Bredt's formula; a change of the Kekulé formula by a modification of Bouveault's process, as the result of an observation by Koenigs.

We shall see by what follows that, personally, Bredt brought forward not a shadow of confirmation of his formula.

The resulting formula for camphoric acid accounted quite well at the time for all the known properties of the acid (oxidation products, interpretation of the different energies of the two carboxyl groups, etc.).

At that moment an event took place which had extremely remarkable consequences. W. A. Noyes[1] showed that β-cam-

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[1] *Loc. cit.*

phoramic acid is converted by bromine and sodium hydroxide into an amino acid, dihydroaminocampholytic acid:

$$C_8H_{14} \underset{CO_2H}{\overset{CONH_2}{<}} \longrightarrow C_8H_{14} \underset{CO_2H}{\overset{NH_2}{<}}.$$

The latter is converted by nitrous acid into an unsaturated acid, campholytic acid, $C_8H_{13}CO_2H$.

This is an α,β-unsaturated acid, for it is reduced by sodium and alcohol to a saturated acid, $C_8H_{15}CO_2H$. The latter, when treated with bromine, takes up the halogen in the α-position and the resulting bromo acid gives again, with potassium hydroxide, campholytic acid. All these facts can be explained only if we assume the presence of the grouping

$$\begin{array}{c} \diagdown \\ C.CH_3 \\ \| \\ -C.CO_2H \end{array}$$
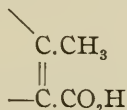
in campholytic acid, and, as a consequence, of the group

$$\begin{array}{c} \diagdown \quad CH_3 \\ C \diagup \\ | \diagdown CO_2H \\ -CH.CO_2H \end{array}$$
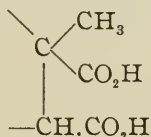
in camphoric acid.

These remarkable experiments, in conjunction with the work of L. Balbiano,[1] who demonstrated the presence of the complex

$$\begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ C \qquad C \diagup^{CH_3} \\ | \qquad \diagdown CO_2H \\ C \end{array}$$
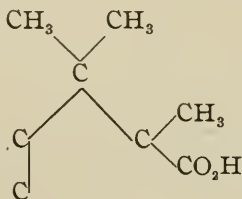
in camphoric acid, led Bouveault to propose a new formula for camphoric acid.

[1] *Rend. Chim. Gen.*, **28**, 1507; Gazz. Chim. Ital., **26**, 1; and *Dict. Chim. Gen.*, **30**, 289, 1901.

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Ber. d. Chem. Ges.

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This formula,
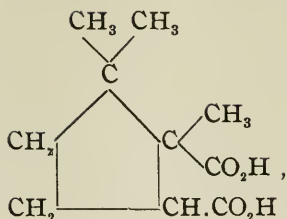
thus obtained, seemed to explain all the more important analytical facts and, consequently, to represent the true constitution of camphoric acid.

My own investigations, which I had undertaken a year before, independently of Bouveault, led me to an identical conclusion.[1]

Camphoric anhydride, treated in chloroform solution with aluminium chloride, yields, by the loss of carbon dioxide, the same campholytic acid which Noyes obtained from β-camphoramic acid; I was able to show definitely and with absolute certainty that this acid had the constitution (I):
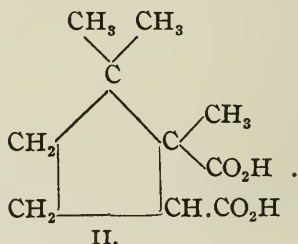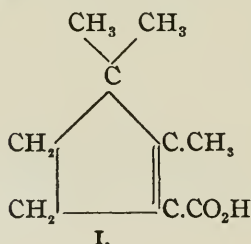
Hence camphoric acid must necessarily be represented by the formula (II).

This point was therefore perfectly cleared up, and the new formula had already secured many adherents when a new article by W. H. Perkin, Jr., on this very point again placed the whole matter in question.[2]

According to W. H. Perkin, Jr., Noyes's campholytic acid

[1] Thesis, Paris, 1899.
[2] J. Chem. Soc., **73**, 796.

does not have the constitution assigned to it by Blanc. It should be represented by the formula (I) and camphoric acid by the formula (II):

$$CH_3 \quad CH_3$$
$$\diagdown \diagup$$
$$C$$

$$CH_2 \diagup \quad \diagdown CH.CH_3$$

$$CO_2H.C \underline{\qquad} CH$$

I.

$$CH_3 \quad CH_3$$
$$\diagdown \diagup$$
$$C$$

$$CH_2 \diagup \qquad C \diagup^{CH_3}_{\diagdown CO_2H}$$

$$CO_2H.CH \underline{\qquad} CH_2$$

II.
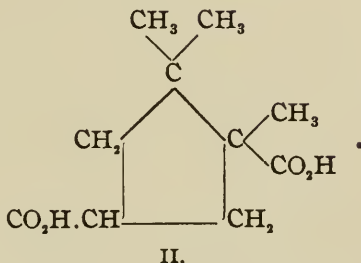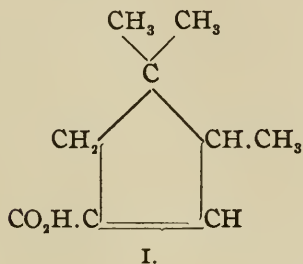
The reasoning adopted by the English chemist was as follows:

When isolauronolic (Noyes's campholytic) acid is oxidized with potassium permanganate, there is formed a keto acid, isolauronic acid, $C_9H_{12}O_3$, whose constitution must be represented by the formula

$$CH_3 \quad CH_3$$
$$\diagdown \diagup$$
$$C$$

$$CH_2 \diagup \qquad \diagdown C.CH_3.$$

$$CO_2H.C \underline{\qquad} CO$$
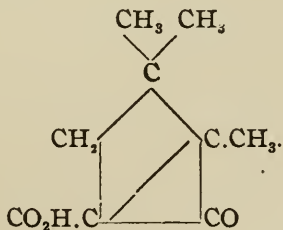
In fact, this acid, when reduced, gives an oxy acid, $C_9H_{14}O_3$ (dihydroisolauronic acid), which does not yield a lactone

and is therefore a β-ketone acid. Moreover, oxidation with chromic acid gives dimethylhexanonoic (dimethylacetyl-butyric) acid, a reaction which Perkin explains as follows:
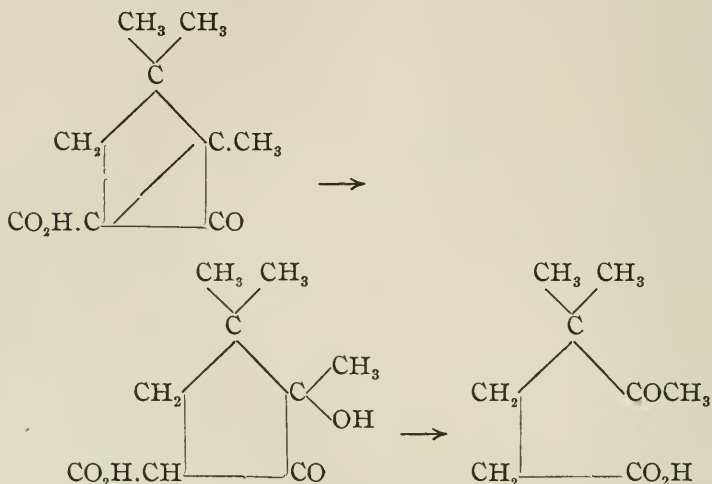
I had no difficulty in showing that this reasoning, as well as the experiments themselves, is vitiated by the gravest errors;[1] that isolauronic acid, far from having the formula assigned to it by Perkin, had, on the contrary, the structure represented by the formula
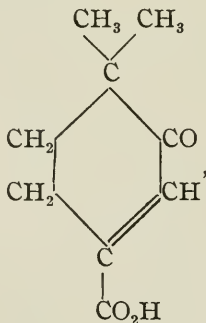
which was perfectly in accord with the formula for isolau-ronolic acid proposed and proved by me:

[1] Bull. Soc. Chim., [3] **21**, 830 (1899).

$$CH_3 \quad CH_3$$
$$\diagdown \diagup$$
$$C$$

CH$_2$ — C.CH$_3$
CH$_2$ — (double bond) C — CO$_2$H $\longrightarrow$

$$CH_3 \quad CH_3$$
$$C$$

CH$_2$ — CO
CH$_2$ — CH$_3$
CO — CO$_2$H $\longrightarrow$

$$CH_3 \quad CH_3$$
$$C$$

CH$_2$ — CO
CH$_2$ — CH
C — CO$_2$H
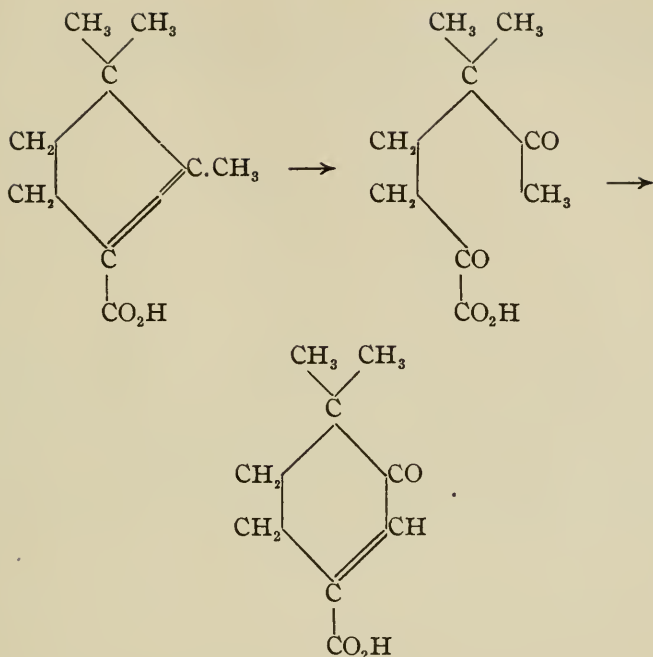
Consequently, Perkin's barely budded formula disappeared, and there remained but those of Bouveault and Bredt, with the greatest chances of probability in favor of the former:

Bouveault's formula.

CH$_3$ CH$_3$ — C
CH$_2$ — C(CH$_3$)(CO$_2$H)
CH$_2$ — CH.CO$_2$H

Bredt's formula.

CH$_3$ CH$_3$ — C
CO$_2$H.CH — C(CH$_3$)(CO$_2$H)
CH$_2$ — CH$_2$
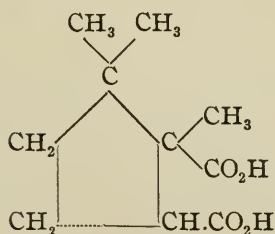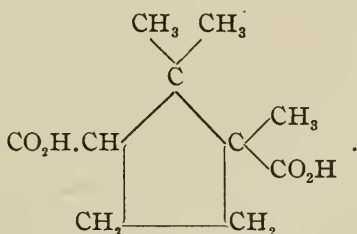
I say chances of probability and not of certainty, for although the most conclusive facts were in its favor (and I repeat that the constitution of isolauronolic acid was a perfectly definite argument), there remained a few points which

had not been cleared up with absolute satisfaction. In the first place it was difficult to see how camphor,
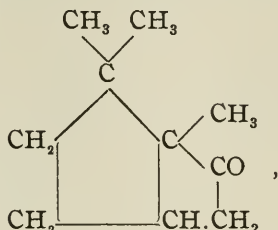
was converted into cymene and carvacrol; again, camphor itself, which must result from the closing of the chain in homo-camphoric acid, would contain a tetramethylene chain, and no such example of ring formation was known.

On the other hand, the difficulty of explaining the lactone nature of camphanic acid,
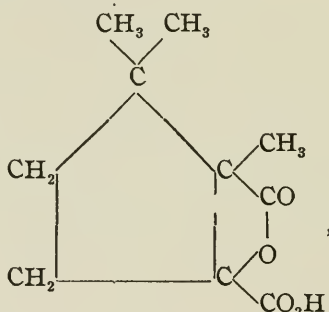
and the oxidation products of α-campholenic acid confirmed my belief as to the necessity of continuing these investigations.

Just at this stage of the problem, Lapworth[1] showed that homocamphoric acid can be brominated and that the bromo acid loses a molecule of hydrobromic acid to form an un-saturated acid which, on oxidation, is converted into oxalic acid and a keto acid, $C_9H_{14}O_3$, camphononic acid:
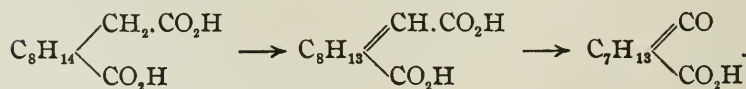
[1] J. Chem. Soc., **77**, 1053.

This acid is stable and is not decomposed by distillation; it can therefore be only a γ- or δ-keto acid. Moreover, by oxidation it is converted into camphoronic acid, which proves its constitution:

Camphononic acid.   Camphoronic acid.
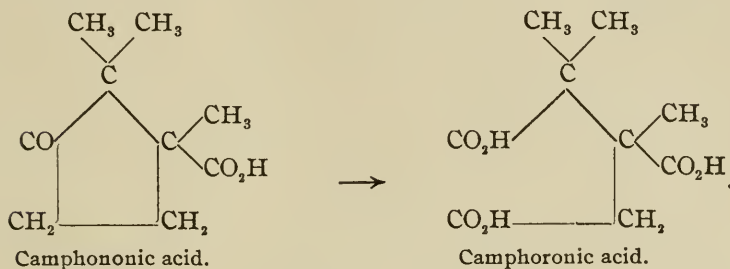
These observations, entirely in harmony with Bredt's formula and totally at variance with Bouveault's, led me to verify again the validity of the reasoning by which I had derived the formula for camphoric acid from the known constitution of isolauronolic acid. I was again unable to find any valid objection against it. If Bouveault's formula was incorrect, then some transformation must necessarily have taken place during the conversion of camphoric into isolauronolic (campholytic) acid.

That this did take place I was, as a matter of fact, able to show. I pointed out,[1] simultaneously with Tiemann,[2] that isolauronolic acid is not the normal product of the decomposition of camphoric acid. The real normal product is a liquid acid (Noyes's *trans*campholytic acid) which is obtained by the action of nitrous acid on dihydroaminocampholytic acid. It is only when finally treated with dilute acids that this compound is transformed, quite easily, to be sure, into a solid crystalline acid (β-campholytic, *cis*campholytic, isolauronolic acid).

This α-campholytic (Noyes's *trans*campholytic) acid is oxidized by nitric acid to dimethyltricarballylic acid, which proves its constitution and, consequently, the correctness of Bredt's formula for camphoric acid:

[1] Bull. Soc. Chim., [3] **25**, 68.
[2] ~~Dict. Chim. Gen.~~, **33**, 2935.
Ber. d. Chem. Ges.

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$$\text{CH}_3 \quad \text{CH}_3$$
$$\text{C}$$
$$\text{CO}_2\text{H.CH} \qquad \text{C} \overset{\text{CH}_3}{\underset{\text{CO}_2\text{H}}{}}$$
$$\text{CH}_2 \text{——} \text{CH}_2$$

$\longrightarrow$

Camphoric acid.

$$\text{CH}_3 \quad \text{CH}_3$$
$$\text{C}$$
$$\text{CO}_2\text{H.CH} \qquad \text{C.CH}_3$$
$$\text{CH}_2 \text{——} \text{CH}$$

$\longrightarrow$

α-Campholytic acid.

$$\text{CH}_3 \quad \text{CH}_3$$
$$\text{C}$$
$$\text{CO}_2\text{H.CH} \qquad \text{CO}_2\text{H}$$
$$\text{CH}_2 \text{——} \text{CO}_2\text{H}$$

Dimethyltricarballylic
acid.
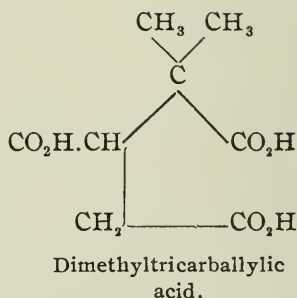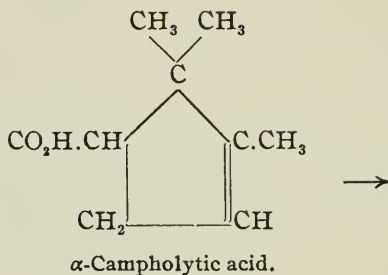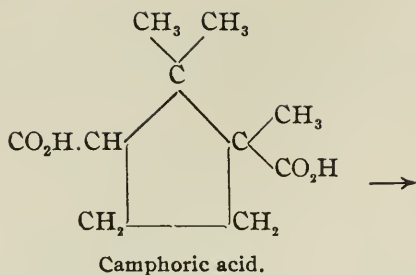
The proof of Bredt's formula is thus due in part to those who had combated it. This is merely mentioned to show that the manifestation of the truth rises above all considerations.

It remains to show how, starting from the constitutional formula for α-campholytic (*trans*campholytic) acid, that of isolauronolic (β-campholytic) acid can be explained. The mechanism of the pinacol reaction shows this very clearly.

CH₃ CH₃ structures...

$$\text{CH}_3 \quad \text{CH}_3$$

First row structures:

CO₂H.CH⟨ ... C.CH₃ / CH₂—CH (with C at top bearing CH₃ CH₃) → CO₂H.CH⟨ ... C⟨CH₃ OH / CH₂—CH₂ →

Second row:

CO₂H.CH⟨ ... C⟨CH₃ CH₃ / CH₂—CH₂ → CO₂H.CH⟨ ... C⟨CH₃ CH₃ / CH₂—CH₂
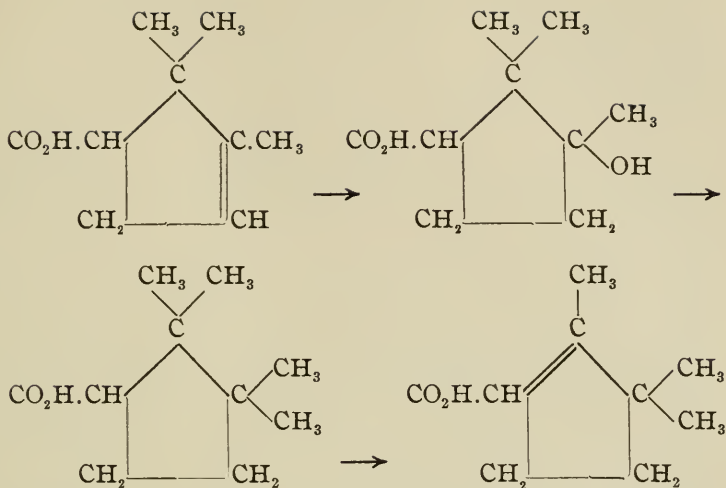
The explanation proposed by Tiffeneau, although leading to the same result, is much simpler and more logical:

CO₂H.CH⟨ ... C⟨OH CH₃ / CH₂—CH₂ → CO₂H.C⟨ ... C.CH₃ / CH₂—CH₂
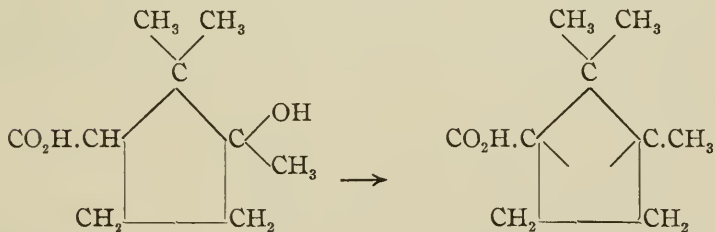
The molecule is thus thrown into a state of unstable equilibrium, and stable equilibrium is established in the simplest possible manner, *viz.*:

CO₂H.CH⟨ ... C.CH₃ / CH₂—CH₂ → CO₂H.CH⟨ ... C⟨CH₃ CH₃ / CH₂—CH₂
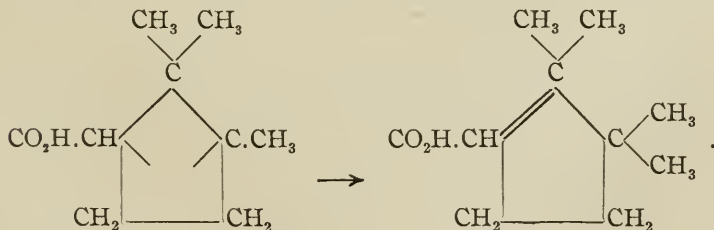
Such are the facts which marked the final adoption of Bredt's formula.

ATTEMPTS TO SYNTHESIZE, AND THE SYNTHESIS OF, CAMPHORIC ACID.

We have just seen the considerable difficulty which those chemists encountered who attacked the problem by analytical methods.

The solution which could not be obtained thus it was sought to obtain by the inverse method, the synthetical. This was a grave mistake, for synthetic investigations in this series are extremely difficult and require an immense amount of work, and it was not till the question had been completely cleared up by the analytical method that two syntheses of camphoric acid were worked out.

For these we are indebted to G. Komppa, on the one hand, and to W. H. Perkin, Jr., and J. F. Thorpe on the other. Of the second of these I shall say nothing except that it is extremely ingenious and that the chemists who effected it gave evidence of remarkable sagacity and patience. Having had occasion to repeat it, I convinced myself that it leads to the result claimed for it.

G. Komppa's Synthesis.[1]

Komppa's synthesis, the first in point of time, attracted considerable attention for, very unjustly, to be sure, the conclusive demonstration of the correctness of Bredt's formula was attributed to it.

Komppa's work, which was never published in detail and has not, in the last six years, passed beyond the stage of a preliminary communication (*vorläufige Mittheilung*), is based on the following facts:

Condensation of oxalic ester with β,β-dimethylglutaric ester:

[1] Dict. Chim. Gén., 36, 4332.

Ber. d. Chem. Ges.

see errata.

v. 45. p. 654

$$
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\diagdown\diagup \\
\text{C} \\
\diagup\qquad\diagdown \\
\text{CO}_2\text{R.CH} \qquad \text{CH.CO}_2\text{R} \\
\\
\text{C}_2\text{H}_5\text{O.CO}\text{———}\text{CO.OC}_2\text{H}_5
\end{array}
\longrightarrow
$$

$$
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\diagdown\diagup \\
\text{C} \\
\diagup\qquad\diagdown \\
\text{CO}_2\text{R.CH} \qquad \text{CH.CO}_2\text{R} \;. \\
\text{CO}\text{———}\text{CO}
\end{array}
$$
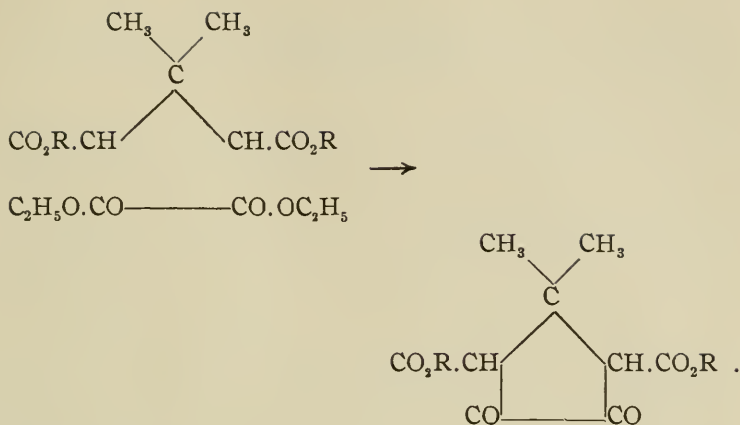
The diketoapocamphoric ester thus obtained is methylated by means of methyl iodide and sodium. The compound sought for is separated first as its sodium, then as its copper salt.

The methylated ester is then reduced with sodium amalgam in water solution in the presence of carbon dioxide:

$$
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\diagdown\diagup \\
\text{C} \\
\diagup\qquad\diagdown \\
\text{CO}_2\text{R.CH} \qquad \text{C}\diagup^{\text{CH}_3}_{\text{CO}_2\text{R}} \\
\text{CO}\text{———}\text{CO}
\end{array}
\longrightarrow
$$

$$
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\diagdown\diagup \\
\text{C} \\
\diagup\qquad\diagdown \\
\text{CO}_2\text{R.CH} \qquad \text{C}\diagup^{\text{CH}_3}_{\text{CO}_2\text{R}} \;. \\
\text{CH}\text{———}\text{CH} \\
| \qquad\qquad | \\
\text{OH} \qquad\quad \text{OH}
\end{array}
$$
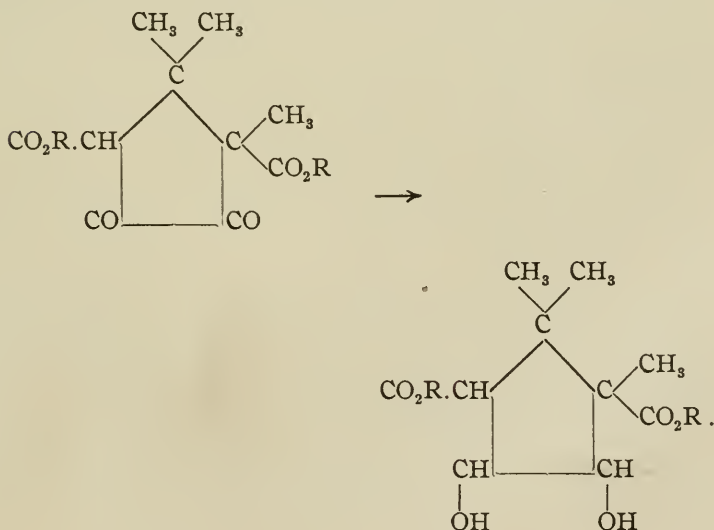
The new product, dihydroxycamphoric ester, is saponified and heated with concentrated hydriodic acid, which gives an unsaturated acid,

$$
\begin{array}{ccc}
\text{CH}_3\ \text{CH}_3 & & \text{CH}_3\ \text{CH}_3 \\
\diagdown\diagup & & \diagdown\diagup \\
\text{C} & & \text{C} \\
\diagup\qquad\diagdown & & \diagup\qquad\diagdown \\
\text{CO}_2\text{H.CH} \qquad \text{C} \diagup^{\text{CH}_3}_{\diagdown\text{CO}_2\text{H}} & \quad\text{or}\quad & \text{CO}_2\text{H.CH} \qquad \text{C} \diagup^{\text{CH}_3}_{\diagdown\text{CO}_2\text{H}} \\
\text{CH}\underline{\qquad\quad}\text{CH} & & \text{CH}\underline{\qquad\quad}\text{CH}_2
\end{array}
$$
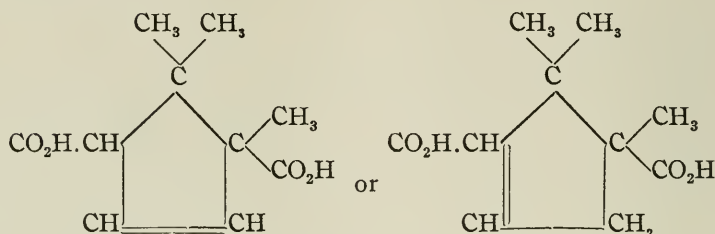
The latter acid can add hydrobromic acid in acetic acid solution, giving a bromcamphoric acid which, by reduction with zinc dust and acetic acid, gives mesocamphoric acid and this, in turn, can be transformed into *cis-r*-camphoric acid.

Such a series of reactions supports with difficulty any serious scrutiny, and from the fact that Komppa has never given the details as to the procedures followed by him and since I have never been able to convert the first cyclic compounds into the diketoapocamphoric acid derivative, I shall consider Komppa's synthesis as nonexistent until the appearance of a detailed report will have enabled me to confirm the reality of a series of reactions which, on paper, offers no great chance of success. This is said merely with the intention of inviting Komppa to hasten the publication of his results.

I have finished this brief historical review of a problem which for several years deeply interested chemists. This question is now and has for some time been absolutely cleared up.

A single point remains in profound darkness; it is the mechanism of the reaction by which camphor passes into camphene, and *vice versa*. This subject therefore deserve ; the attention of those whom difficult investigations do not deter.

Perhaps I shall some day have the opportunity to take it up.

OBITUARIES.

Dr. Charles B. Dudley, Chief Chemist of the Pennsylvania Railroad, died of pneumonia after a very short illness on December 21st, 1909, at his home in Altoona, Pa. By his death chemistry loses one of its most enthusiastic supporters, science a devoted advocate, industry an important adviser, the country a patriotic citizen, and many in all professions a devoted and true friend.

Dr. Dudley was born at Oxford, Chenango Co., N. Y., July 14, 1842, of New England parentage. His early days were spent in attending the village school during the winter and in work upon the farm during the summer. In 1862 his patriotic spirit led him to enlist in the One Hundredth and Fourteenth Regiment of New York Volunteers, and he spent the greater part of the three succeeding years in the service of his country, taking part in seven battles and finally being wounded September 19, 1864, in the battle of Opequan Creek in the Shenandoah campaign. After his return from the war he continued his preparation for college at Oxford Academy. He entered Yale College and graduated with the class of 1871. The next year he spent in newspaper work in New Haven, and in this manner saved enough to enable him to pursue further studies in chemistry and physics in the Sheffield Scientific School, from which he received the degree of Ph.D. in 1874. The year following was spent as assistant in physics, under Prof. Barker, at the University of Pennsylvania. In the fall of 1875 he accepted the position of teacher of science in Riverview Military Academy, Poughkeepsie, N. Y., but remained only a month, leaving to accept the position of chemist with the Pennsylvania Railroad. From that time until his death he was continuously connected with this company. He was married April 17, 1906, to Mary V. Crawford, of Bryn Mawr, Pa.

Dr. Dudley was essentially a pioneer in the field of testing materials, and during his thirty-four years of service he accomplished an enormous amount of work, remarkable improvements were made for his company, and the world has adopted many of his recommendations as standards. A man of strong character, high ideals, clear, calm judgment, scholarly attainments, and a rare combination of qualities—charming personality, sympathetic, optimistic, he was unusually well

fitted for his task. After the organization of the laboratory, and establishing such routine testing as could be done at the time, be began a series of investigations upon the various materials used in railway practice. The investigations soon led to the introduction of specifications for the purchase of material, and these specifications, giving in some cases standard methods of analysis, have been widely copied, and have been very largely adopted as standards throughout the country. In this pioneer work, and always in all subsequent work, he was most zealous to protect the interests of his company, but at the same time he was always just to the manufacturer. He never expected the impossible of the manufacturers, but invariably led them persistently and tactfully toward his own high ideals. His views of the immediate needs of the Pennsylvania Railroad and the ultimate need of the world at large were so broad that he succeeded not only in safe-guarding the interests of his company and protecting the lives of its employees and passengers but in raising the standards of all the manufacturers having dealings with the company. The work of his laboratory on oils, paints and varnishes, bronzes and bearing metals, the various classes of steel used in locomotive and car construction, cast iron for car wheels, water examination, car ventilation and sanitation, the transportation of explosives, etc., marks an important epoch in the history of applied chemisty in America.

The first work which attracted attention to the Altoona laboratory was upon "The Wearing Capacity of Steel Rails in Relation to Their Chemical Composition and Physical Properties," which appeared in 1881. This paper not only had the effect of bringing to the attention of the world the need of a good quality of steel for rails, but what the author most desired, it focused the attention of metallurgists and engineers upon an important problem, and created discussion. Such discussion, whether favorable or otherwise, Dr. Dudley always thought of the greatest importance and he gladly welcomed it. Subsequent papers on the constitution of cast iron, and upon the qualities of bearing metals led to improvements in the manufacture of car wheels and to increased efficiency in bearings. Papers on oils, paints, and analytical methods all seemed to show the need for the improvement of these products or the means of testing them. Unfortunately, the publications from this laboratory were all too few because of the pressure of routine work in most varied fields, but part of his wonderful experience is related in his presidential addresses before the American Society for Testing Materials, and in discussions before this and other societies.

He was always an active worker in the interests of the American Chemical Society, for some time a councilor, and for two years president of the society. He was also a member of the English, French and German chemical societies.

Since 1902 he had been president of the American Society for Testing Materials, and last August, at the Stockholm meeting, was elected for a term of three years president of the International Society for Testing Materials. Of the former society he had been the heart and soul. His presidential addresses were models of their kind, and as presiding officer he brought out full discussion, and by his geniality and tact harmonized all interests.

Dr. Dudley was also president of the Bureau of Safe Transportation of Explosives and other Hazardous Materials of the American Railway Association, and gave much of his time during the past two years to the study of explosives and their safe handling in transportation. The catholicity of his tastes and his wide interests is shown in the large number of societies of which he was a member. He belonged to the American Societies of Civil, Mechanical, Mining, Sanitary and Electrical Engineering, the American Philosophical Society, American Historical Society, Society for the Promotion of Engineering Education, American Public Health Association, the Iron and Steel Institute of Great Britain, and others.

Dr. Dudley accomplished a great work. He was a broad-minded, widely educated man of simple and refined tastes, a true and faithful friend, and he was beloved by all who had the privilege of knowing him. Henry Fay.

JAKOB VOLHARD.

Jakob Volhard, professor at the University of Halle, died on the 14th of January in his 76th year. He was a many-sided man; as investigator, as teacher, as editor and as biographer he showed great ability.

Volhard was born in Darmstadt, June 4th, 1834. His father was a lawyer and an intimate friend of Liebig, whose influence led young Volhard to the study of chemistry. Entering Liebig's laboratory in Giessen, in 1852, he studied under Liebig, Will and Kopp, receiving his doctorate in 1855. After working with Bunsen in Heidelberg for some time, he became Liebig's assistant in Munich, but in 1860 joined A. W. von Hofmann, in London. His studies of substituted ureas was made in Hofmann's laboratory. In 1862, while working in Kolbe's laboratory in Marburg, he published his

well-known synthesis of sarcosine. In 1863 he became privat-dozent in Munich with Liebig, who assigned to him the lectures in organic chemistry. In 1868 he published the synthesis of creatine. He was made professor-extraordinarius in 1869.

After Liebig's death Adolf von Baeyer was called to Munich to reorganize the chemical department, and the new laboratory was built; it was the largest and best equipped at the time, and students poured in. The inorganic department was given to Volhard, and a new chapter of his life-work began. His studies with Bunsen bore fruit; turning his back upon organic chemistry, his lectures, his teaching and his private work were given to inorganic, and specially to analytical chemistry. His volumetric methods for the determination of silver, his introduction of ammonium sulphocyanide in volumetric work, his determination of manganese and his iodometric determination of sulphurous acid are now classic methods known in every laboratory.

It was, however, not as investigator, but as teacher, that Volhard showed his greatest power. Those who had the privilege of studying under his guidance during this period felt the constant inspiration of his teaching in the laboratory; his lectures on that usually dull subject, analytical chemistry, were masterly, and the students listened with breathless interest. His little book, "Introduction to Chemical Analysis," written at this time, is still in use in many German and some American laboratories.

It may be asked, if Volhard was so great a teacher of inorganic chemistry, where are his pupils? At this period nearly all young men of ability preferred organic chemistry as life-work, and their contact with Volhard was brief. Of the few who elected inorganic chemistry, the most promising perhaps were Clemens Zimmermann and Gerhard Krüss. Both died very young, each having done enough to earn a place in the annals of analytical chemistry and to show the result of Volhard's teaching.

In 1871 Volhard succeeded Liebig as editor of the "Annalen," and continued this work with energy and success for nearly forty years. In 1879 he accepted the chair of chemistry at Erlangen, and in 1882 went to Halle, where he conducted the chemical department till 1908, when he retired from active work.

Volhard's marked artistic and literary taste was of service in his biographical work. In 1870 he published "The Foundation of Chemistry by Lavoisier," and in this his anti-French

and strong German feeling is clearly shown. In 1902 he wrote his beautiful life of Hofmann and in 1909 he published his great biography of Liebig, a delightful book which has received the highest praise from all critics.

Volhard's personality was marked; his frame was almost gigantic; his noble leonine head towered above ordinary men. Students first approached him with a sensation of fear, which soon gave place to admiration. Those who knew him well delighted in his conversation replete with wit, humor and knowledge, no matter what subject was broached. He was the last of the distinguished pupils of Liebig and Liebig's contemporaries—the last of the old guard. E. RENOUF.

REVIEWS.

VERHALTEN DER WICHTIGSTEN SELTENEN ERDEN ZU REAGENTIEN. Zum Gebrauch im Laboratorium. VON DR. JOS. V. PANAYEFF, vorm. Dozent am Chemischen Laboratorium Fresenius zu Wiesbaden. Halle a. S. : Druck und Verlag von Wilhelm Knapp. 1909. pp. iv + 83. Price, M 3.60.

This little book is well characterized by its title, which in itself is a practical review of its contents. Dr. von Panayeff has gathered together and given with some detail the action that takes place when soluble zirconium, thorium, cerium, praseodymium, neodymium, lanthanum, yttrium and erbium salts are treated with reagents. The compilation appears to have been accurately done by one familiar with the work from close personal observation, and some reactions original with the author are added. Each metal considered is first carefully described in the elementary stage so far as it has been obtained pure, but no serious attempt is made to point out methods of separation. The book is just what it pretends to be. CHARLES L. PARSONS.

A SHORT HANDBOOK OF OIL ANALYSIS. BY AUGUSTUS H. GILL, S.B., Ph.D., Associate Professor of Technical Analysis at the Massachusetts Institute of Technology, Boston, Mass. Fifth edition, revised and enlarged. Philadelphia and London: J. B. Lippincott Company. 1909. pp. 179. Price, $2.

The fifth edition of Gill's "Handbook of Oil Analysis" with its revision to include present practice will be welcomed by all who are interested in the examination of oils, for the usefulness of the previous editions has been widely appreciated. It is a great convenience to have at hand, in a concise form, such a collection of well-tried methods of tests and examination, but sufficiently comprehensive in its scope for ordinary

practical use. Besides the methods of analysis, mineral, animal, and vegetable oils are described as to their source, properties and uses. The appendix includes well-selected tables, a useful description of reagents, and a statement of commercial specifications.

The author's opinion as to the doubtful value of frictional journal tests will doubtless not be shared by those who appreciate their practical advantages. CHARLES F. MABERY.

ELEMENTARY MODERN CHEMISTRY. BY WILHELM OSTWALD, Emeritus Professor of Chemistry in the University of Leipzig and HARRY W. MORSE, Instructor in Physics in Harvard University. Boston, New York, Chicago, London: Linn & Co. pp. x + 290. Price, $1.

Every book by Ostwald has a touch of his genius and differs from the ordinary run of text-books. This little volume seems to be intended for schools; it would form an almost ideal preparation for college work. Following the ordinary sequence of elementary inorganic text-books, Ostwald explains combining weights, atoms, molecules, gram-molecular weights, electrolysis and electrolytic dissociation in such a lucid and simple way that any intelligent school boy would follow his reasoning. Indeed, the book would suffice admirably for a first year's college work in connection with lectures and some book for reference and study giving additional facts; this would be necessary, because—perhaps to gain space for theory—the amount of chemical fact in the book is reduced to a minimum: one example may suffice; steel is so defined as to lead to the belief that it is a substance differing from wrought iron or cast iron by its carbon percentage alone; nothing is said of it properties.

The book is illustrated with admirable diagrams and also contains portraits of Priestley, Ramsay, Dalton, Faraday, Berthelot, Bunsen, Willard Gibbs and Berzelius.

How much of the praise given Ostwald is due to Mr. Morse is doubtful, as the degree of Mr. Morse's collaboration is not stated; the qualities praised, however, are equally noticeable in Ostwald's former elementary book, "Conversations on Chemistry." E. R.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

On the evening of February 3, 1910, an informal gathering took place at which there were present, among others, most of those to whom had been delegated the task of providing for the creation of an organization for the Eighth

International Congress of Applied Chemistry, by the London Congress last June; a representative of the Association of Manufacturing Chemists, the American Chemical Society, the American Electrochemical Society, the Society of Chemical Industry were each also present at this informal meeting.

The concensus of opinion was that the greatest success could be expected only if the most effective system and mode of organization could be had, and if each and every chemist in the United States could be made to feel that he himself directly or indirectly, through his professional, business or educational affiliations, had a personal share of responsibility in the conduct and management of the Congress from its very start and to its very end. This was regarded as the proper and correct guide in proposing any plans or schemes of organization.

The Eighth Congress is to convene in 1912, with Professor Edward W. Morley as honorary president and Dr. W. H. Nichols as acting president, at a time and place to be determined by the Organization of this Congress. The most important part of the Congress, in fact that by which its value and real success will be measured, is the amount of original matter, both scientific and technical, which it will be able to present to its members. To this end, every chemist in America who has or may have any original matter to present to this Congress should begin without delay to prepare such matter, and have it in shape so that it may be presented to the Congress in ample time for proper printing, classification and distribution to members and the technical and scientific press.

The Congress, being held in the United States, will with a great deal of right and naturally look to a very good showing from the chemists of the United States, and every chemist in this country, which is to be host to our foreign colleagues, should constitute himself a committee of one to get from himself, or from his friends, as much scientifically or technically valuable material as possible, so that the proceedings and publications of the Eighth Congress may correctly reflect the true mental attitude of the chemists of the United States towards their profession, both as a pure science and as a part of the industrial activities of this country.

It is the hope that the Program Committee will be able to begin its activities effectively before the close of 1910, but in the meantime it behooves every chemist in the United States actively and energetically to consider how and in what way he can best contribute to the success of this Congress, and particularly in the direction of papers and communications

to the Congress embodying the advance in this field since June, 1909, the date of the last Congress.

At a meeting to be held in April or May, 1910, by those charged with the duty of providing suitable organization for the Eighth Congress, some definite action as to such organization may be looked for.   Those who have that responsibility are making every effort to get as many suggestions as to divisions of organization, mode of organizing and membership of the organization as possible. . Every one interested in having this organization on as broad foundations as possible is earnestly invited to present any suggestions that may be helpful in that direction, in writing, by the middle of April, 1910, so that all these suggestions may be properly classified and collated and put in condition for most thorough consideration before the meeting above referred to actually takes place. Such communications may be addressed to the Temporary Secretary, Gr. B. C. Hesse, 90 William Street, New York City.

AMERICAN

CHEMICAL JOURNAL

VISCOSITY AND FLUIDITY.

[NINTH COMMUNICATION BEARING ON THIS SUBJECT.]

By EUGENE C. BINGHAM.

In a recent paper[1] by the author it was shown that the simple formula,

$$t = A\varphi - B/\varphi + C,$$

can be used to represent fluidity data with an ease and accuracy unequalled by any formula heretofore proposed. This formula was derived from the fundamental assumption that, for the ideal liquid, fluidities are directly proportional to the absolute temperature. The following facts have led the author to the belief that the above hypothesis is now fairly substantiated.

1. This hypothesis admits of a simple physical explanation, as already pointed out,[2] on the basis of the kinetic theory. Fluidity and viscosity are the exact analogues of conductance and resistance, respectively, in electricity. The alternate hypothesis that viscosities are additive, which has been held until recently, does not permit of a simple physical conception.

[1] Bingham: Z. physik. Chem., **66**, 238 (1909). THIS JOURNAL, **40**, 277 (1908).
[2] Bingham: THIS JOURNAL, **35**, 195 (1906).

2. It has already been shown by many investigators[1] that there is, in fact, a parallelism between fluidity and conductivity. This would be unintelligible under the old assumption.

3. The fluidities of mixtures of liquids, where there is no marked temperature or volume change on mixing, are additive, as the hypothesis demands.[2]

4. The fluidities of unassociated liquids are, to a marked degree, directly proportional to the temperature. Even associated compounds appear to behave similarly at high temperatures.[3]

5. By comparing fluidities, instead of viscosities, new relations are brought out between fluidity and other physical properties. For example, the fluidities of all of the aliphatic hydrocarbons are nearly identical at their boiling points. The same is true for the ethers, and a simple relation exists between the fluidities of other classes, as iodides and bromides, at their boiling points. These relations do not make themselves evident when viscosities are compared, as has been done heretofore.

6. One of the most convincing arguments in favor of the hypothesis lies in the fact that the best results obtained in comparing viscosities have been at temperatures (or viscosities) of *equal slope*. This is precisely the same as comparing temperatures of equal fluidity *for a given class of compounds*, as I have shown.[4] But comparing temperatures (or viscosities) of equal slope on the viscosity curves does not give satisfactory results for *different classes* of compounds. Thus oxygen has a different value in each class. But when fluidities are compared the value of oxygen is the same in all classes of compounds. I believe that the same is true of the other atoms and groups. It seems to be something like a confession of ignorance of the property dealt with, when we assume a definite value for an atom or group and then find it necessary to change that value for every class of compounds.

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[1] Jones and Bingham: Z. physik. Chem., **57**, 237 (1906). This Journal, **34**, 547 (1905). Bingham: Diss., Johns Hopkins, 1905, p. 71.

[2] Bingham: This Journal, **35**, 214 (1906).

[3] Bingham and Miss Harrison: Z. physik. Chem., **66**, 2 *et seq.* (1909).

[4] *Ibid.*, p. 19 *et seq.*

7. Furthermore, by comparing fluidities, it is possible to get a measure of association[1]—a thing which has never before been attempted, so far as is known to the author, by the analysis of viscosity data according to the older conception.

8. The fact that a simple equation, derived from the use of the above hypothesis, excels the equations heretofore proposed to represent viscosity data and that with a slight modification it will represent the observed values to nearly the limits of experimental error, is evidence in itself, and when taken in connection with the other facts mentioned above or to be found in the papers already referred to, it seems to make the evidence sufficiently strong to permit the provisional acceptance of the hypothesis, until facts arise which shall call it again into question and make worth while the search for further direct evidence. In the meantime it will be used for further investigation.

If the above view is correct, it is important that it become established as speedily as possible. For, as already pointed out, the view that viscosities are additive, which is still current, has led investigators to very erroneous conclusions. Moreover, it keeps viscosity (or its reciprocal, fluidity) from assuming its proper importance among the physical properties, the property being scarcely discussed in our text-books. Yet the laws of viscosity are doubtless fundamental in the understanding of conductivity in solution, ionic migration, diffusion, velocity of reaction, association; and viscosity is intimately connected with still other properties, such as vapor pressure and cubical expansion.

The author has already discussed some of these connections on the hypothesis that fluidities, *and not viscosities*, are additive. Others will be discussed in this and succeeding papers.

FLUIDITY FORMULAS.

In an early paper[2] I suggested the use, for the representation of viscosity data, of a formula of the form

$$\varphi = c/(\varphi - at - b),$$

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[1] Bingham and Miss Harrison: Z. physik. Chem., **66**, 26 *et seq.* (1909).
[2] This Journal, **35**, 216 (1906).

where φ represents fluidity, t temperature, and a, b, and c are constants. This formula was suggested to me in a conversation with Dr. A. B. Coble, of the Johns Hopkins University, while discussing the mathematical properties of a fluidity curve according to my hypothesis. Later, I derived the formula

$$t = A\varphi - B/\varphi + C,$$

which proved capable of representing viscosity data with fidelity, and the earlier formula was lost sight of. It is worth while to note, however, that both are reducible to the same form when $A = 1/a$, $B = c/a$, and $C = -b/a$.

Volume.

It is interesting to note that van der Waal's equation,

$$\left(p - \frac{a}{v^2}\right)(v - b) = RT,$$

gives

$$T = \frac{p}{R}v - \frac{pb}{R} - \frac{a}{Rv} + \frac{ab}{Rv^2},$$

which, when the pressure is constant, is the same as my simpler formula, with the exception of the amplifying term $\frac{ab}{Rv^2}$, and of the sign of the constant $\frac{pb}{R}$, which may be dependent upon the dimensions of the units employed. It would not be very surprising, perhaps, if some intimate relation could be established between volume and fluidity, and there is every reason why the question should be investigated. The above formula can easily be tested in the simpler form,

$$T = \alpha\varphi - \beta - \frac{\gamma}{\varphi} + \frac{\delta}{\varphi^2},$$

where α, β, γ, and δ are constants. This has been done for a number of substances to which my simple formula did not apply very well and also for octane. The result is shown in the following tables. The data used are those furnished by the viscosity observations of Thorpe and Rodger and

already used by me in testing my other formulas. To save space only the observed temperatures and those calculated by the formula are given, together with the percenatge differences.

The equations used in calculating the constants are the following:

$$= \frac{t_2 - t_1}{\varphi_2 - \varphi} - \frac{\gamma}{\varphi_1 \varphi_2} + \frac{\delta(\varphi_1 + \varphi_2)}{\varphi_1{}^2 \varphi_2{}^2}$$

$$= t_1 + \frac{\gamma}{\varphi_1} - \frac{\delta}{\varphi_1{}^2} - \alpha \varphi_1$$

$$= \frac{\dfrac{t_3 - t_2}{\varphi_3 - \varphi_2} - \dfrac{t_2 - t_1}{\varphi_2 - \varphi_1} - \delta\left(\dfrac{\varphi_1 + \varphi_2}{\varphi_1{}^2 \varphi_2{}^2} - \dfrac{\varphi_2 + \varphi_3}{\varphi_2{}^2 \varphi_3{}^2}\right)}{\dfrac{1}{\varphi_2 \varphi_3} - \dfrac{1}{\varphi_1 \varphi_2}}$$

$$= \frac{\left(\dfrac{t_3 - t_2}{\varphi_3 - \varphi_2} - \dfrac{t_4 - t_3}{\varphi_4 - \varphi_3}\right)\left(\dfrac{1}{\varphi_1 \varphi_2} - \dfrac{1}{\varphi_2 \varphi_3}\right) - \left(\dfrac{t_2 - t_1}{\varphi_2 - \varphi_1} - \dfrac{t_3 - t_2}{\varphi_3 - \varphi_2}\right)\left(\dfrac{1}{\varphi_2 \varphi_3} - \dfrac{1}{\varphi_3 \varphi_4}\right)}{\left(\dfrac{\varphi_1 + \varphi_2}{\varphi_1{}^2 \varphi_2{}^2} - \dfrac{\varphi_2 + \varphi_3}{\varphi_2{}^2 \varphi_3{}^2}\right)\left(\dfrac{1}{\varphi_2 \varphi_3} - \dfrac{1}{\varphi_3 \varphi_4}\right) - \left(\dfrac{\varphi_2 + \varphi_3}{\varphi_2{}^2 \varphi_3{}^2} - \dfrac{\varphi_3 + \varphi_4}{\varphi_3{}^2 \varphi_4{}^2}\right)\left(\dfrac{1}{\varphi_1 \varphi_2} - \dfrac{1}{\varphi_2 \varphi_3}\right)}$$

where t_1, t_2, t_3, and t_4 are observed temperatures corresponding to the fluidities φ_1, φ_2, φ_3, and φ_4, respectively.

Table I.—*Water.*

$\alpha = 0.24542$, $\beta = 296.15$, $\gamma = 3751.8$, $\delta = 94508$.

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.37	273.37	0.00	312.32	312.52	+0.06
274.13	273.99	—0.05	320.03	320.28	+0.07
276.09	275.53	—0.20	328.53	328.71	+0.05
277.47	276.82	—0.23	337.01	337.01	0.00
278.45	277.62	—0.29	345.54	345.60	+0.02
281.01	280.23	—0.27	353.75	353.72	—0.01
286.53	285.80	—0.25	362.90	362.77	—0.03
295.02	294.64	—0.13	371.09	371.02	—0.02
303.72	303.72	0.00	373.00	373.00	0.00

Average, 0.09

Table II.—Octane.

$\alpha = 0.19074, \beta = 343.42, \gamma = 23,193, \delta = 1,325,100.$

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
373.25	273.25	0.00	339.46	339.75	+0.08
285.18	284.52	—0.23	350.82	350.82	0.00
295.92	295.33	—0.19	361.33	361.52	+0.05
305.96	305.63	—0.10	371.52	371.30	—0.05
316.89	316.88	0.00	382.07	381.57	—0.13
327.73	328.12	+0.11	395.07	395.05	0.00

Average,   0.08

Table III.—Isobutyric Acid.

$\alpha = 0.31190, \beta = 354.27, \gamma = 10,279, \delta = 276,425.$

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
276.69	276.69	0.00	361.06	361.07	+0.00
290.00	287.53	—0.08	371.94	372.37	+0.11
302.33	300.57	—0.58	382.78	383.05	+0.07
315.53	314.88	—0.20	395.97	393.65	—0.08
327.54	327.55	+0.00	407.50	407.16	—0.08
343.49	343.93	+0.12	420.47	420.51	+0.01

Average,   0.11

Table IV.—Active Amyl Alcohol.

$\alpha = 0.26970, \beta = 335.66, \gamma = 1425.7, \delta = 7618.7.$

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.40	273.40	0.00	340.52	339.30	—0.06
284.63	279.36	—1.85	352.25	352.25	0.00
296.30	292.60	—1.24	364.88	363.31	—0.43
307.75	307.75	0.00	373.03	372.04	—0.26
320.40	322.13	+0.53	385.78	384.58	—0.31
329.94	329.62	—0.09	397.36	397.36	0.00

Average,   0.38

The results of Tables I–IV show that van der Waal's equation may be used to reproduce fluidity data somewhat better than my simpler formula containing only three constants, but not nearly so well as my modified formula containing

four constants. Table V, giving the average percentage differences for the above compounds, will make this clearer.

Table V.—Average Percentage Differences from Using the Equa-

$$tions \ (1) \ t = A\varphi - \frac{B}{\varphi} + C, \ (2) \ t = A\varphi - \frac{B}{\varphi + D} + C,$$

$$and \ (3) \ T = \alpha\varphi - \beta - \frac{\gamma}{\varphi} + \frac{\delta}{\varphi^2}.$$

Substance.	Average per cent. difference from (1).	Average per cent. difference from (2).	Average per cent difference from (3).
Water	0.17	0.01	0.09
Octane	0.16	0.02	0.08
Isobutyric acid	0.43	0.06	0.11
Active amyl alcohol	1.17	0.08	0.38

On the one hand, we must recall that van der Waal's equation does not hold satisfactorily for volume, therefore the inferior agreement here exhibited does not prove that there is not an intimate relation between volume and fluidity. On the other hand, we recognize perfectly that such a relation would not be *proved* even if the same equation did hold accurately for both properties. My intention, at this time, is merely to call attention to the coincidence, and to try out formulas other than those already proposed.

The Abnormal Expansion Coefficient of Water at 4°.

With the purpose of testing further the possibility of a relationship between fluidity and volume, I made a study of the viscosity data of Thorpe and Rodger in the vicinity of 4°. They worked with special care and precision around this point with water, trying to detect abnormalities, but they were unable to detect any and properly point out that "the anomalous change in the density of water amounts to only 1 part in 10,000," hence one would hardly expect to find a maximum or minimum in so steep a curve as the fluidity curve. One would look only for a sagging or heaving in the curve. But as already noted, my modified equation holds for water with extreme accuracy, better, in fact, than for any other associated compound. Table VI gives the values

of the observed temperatures in the region of 4°, using the constants already calculated for water between 0° and 100°. Of the temperatures given in Table VI only one, marked with a (*), was used in deriving the constants:

Table VI.—Water.

$$A = 0.23275, B = 8676.8, C = 309.17, D = 120.00.$$

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.37*	273.37	0.00	277.47	277.46	—0.00
274.13	274.18	+0.02	278.19	278.19	0.00
274.86	274.87	+0.00	278.94	278.99	+0.02
275.41	275.43	+0.01	279.67	279.69	+0.01
276.09	276.03	—0.02	280.41	280.46	+0.02
276.84	276.81	—0.01	281.01	281.04	+0.01
				Average,	0.01

The correspondence between the calculated and observed values is truly remarkable, the more so when we examine carefully the calculated curves for other associated substances.[1] There we see that in reference to the first, middle, and last observations used in getting the constants, the calculated values of the temperature are usually first too small, then too large, and then again too small. In other words, my modified equation gives a curve which is probably invariably very slightly too sharply bent. The differences between the calculated and observed values, to be sure, are almost to the limit of experimental error, but *not quite.* If this is true, then water is exceptional among associated liquids in that at low temperatures the observed values of the temperature are smaller than would be expected. There is, therefore, in the case of water, a decrease in fluidity in the neighborhood of 4° to an amount of the same magnitude as the decrease in volume. It seems likely that this point could be definitely settled by applying my modified formula to a larger number of substances and proving that there is a constant deviation between the calculated and observed values as indicated.

[1] Z. physik. Chem., **66,** 252 and 253 (1909).

Critical Temperature.

It is a necessity of the human mind that the simplest relations appear first and that as the range of vision increases the complexity of phenomena becomes manifest. Thus, although we may grope for some simple relation between volume and fluidity at ordinary temperatures, we must recognize that over a broad range of temperature the relation cannot be entirely simple. Instead of fluidity continually increasing as the volume and temperature increase, the fluidity must pass through a maximum, since in gases the fluidity decreases with the temperature. There is no reason, however, for being disturbed over this fact since in liquids the viscosity is probably caused largely by the attraction between the particles, and in gases by the kinetic energy of the particles, and therefore we cannot expect a simple law to apply to both states of matter. It will be interesting to learn whether the maximum in fluidity is connected with the critical temperature. There seem to be no data on this point.

Vapor Pressure.

The fact that the fluidities of saturated aliphatic hydrocarbons and of ethers are for each class practically identical at the boiling points of the substances suggested the question as to whether this remarkable relation holds for other temperatures of equal vapor pressure. The data of Young and his collaborators enable us to give a partial answer to this question. The fluidity data are taken from the tables of Bingham and Miss Harrison,[1] as calculated from the viscosity data of Thorpe and Rodger. The fluidities and vapor pressures corresponding to every 10° of temperature, as given in Table VII, were plotted against each other and the result is seen in Figure I, where ordinates represent fluidities and abscissas vapor pressures in millimeters:

[1] Z. physik. Chem., **66,** 13 (1909).

Table VII.—*Fluidities and Vapor Pressures of Aliphatic Hydro-carbons for Every 10°.*

	Pentane.		Hexane.		Heptane.		Octane.	
Temp.	φ.	p. Young.	φ.	p. Thomas and Young.	φ.	p. Young.	φ.	p. Young.
0	353.4	183.25	252.3	45.45	192.4	11.45	142.1	2.94
10	391.2	281.8	281.8	75.00	217.5	20.50	163.4	5.62
20	430.8	420.2	312.4	120.0	243.6	35.50	185.9	10.45
30	472.1	610.9	344.8	185.4	271.2	58.35	209.1	18.40
40	(513.6)	873.0	378.8	276.7	299.5	92.05	233.6	30.85
50			414.9	400.9	329.9	140.9	259.4	49.35
60			452.7	566.2	362.1	208.9	286.4	77.55
70			(494.6)	787.0	395.0	302.3	314.5	117.9
80					431.0	426.6	344.3	174.8
90					468.3	588.8	376.2	253.5
100					(511.2)	795.2	409.0	353.6
110							443.5	481.9
120							482.0	646.4
130							(523.0)	859.0
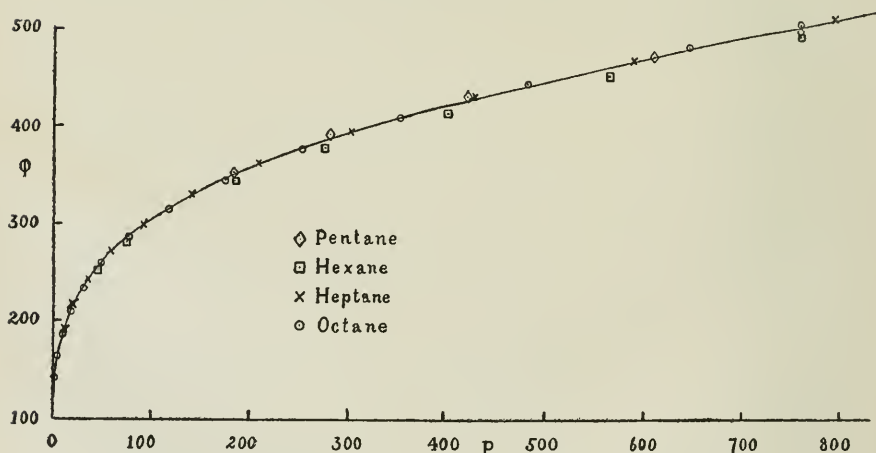
Figure I.—fluidity-vapor pressure curve of the aliphatic hydrocarbons.

It is seen that the fluidity-vapor pressure curves of the available aliphatic hydrocarbons lie closely together. This extraordinary result proves that fluidity and vapor pressure are closely related, presumably due to the fact that both are

dependent upon the intermolecular forces. Since the fluidity-vapor pressure curve becomes continually more and more nearly linear it is worth while to point out that probably for very high fluidities the vapor pressure is directly proportional to the fluidity.

EXPERIMENTAL.

Having reached the above results with the data at hand, it became highly desirable to measure the vapor pressures of the ethers whose fluidities were known in order to see in how far they behave like the hydrocarbons. This work was done at the University of Chicago during the summer of 1909, and I am highly indebted for the courtesy shown me there and for the use of apparatus from both the Kent Chemical Laboratory and the Ryerson Physical Laboratory.

In measuring vapor pressure, the dynamical method of Ramsay and Young[1] was used. However, as ethers were to be used, rubber connections were avoided wherever the ether would come into contact with them. A small dropping funnel with glass stopcock and stopper was used. The joints were ground with the finest emery until they were close-fitting, and stopcock grease could be avoided. A trace of phosphoric acid was occasionally used as a lubricant, but generally the ethers themselves served for this purpose, and to keep air from leaking in. The tube of the dropping funnel was properly bent and drawn out to deliver the ether on cotton wound on the stem of a thermometer. The cotton was extracted with ether, dried and kept in a desiccator until used. The thermometers were of the Gerhardt type, nitrogen-filled. They were tested by immersion in ice and in a boiling-point apparatus for testing thermometers, and the corrections were applied to all observations. One thermometer extended from —5° to 55° and the other from 45° to 105°. The ends of the dropping funnel and the thermometer were forced through two holes in a good cork and the whole tightly fitted into a large test tube, to which had been sealed a side tube leading to a receiver. The test tube was heated by means of a bath

[1] J. Chem. Soc., **47**, 42 (1885).

consisting of a large beaker of water, which was stirred. The receiver was cooled with a mixture of ice and salt. From the receiver a tube led to the manometer, made especially for this purpose by Boehm & Co. It consisted of an $\cup$-tube, one end of which was closed, filled with freshly-distilled mercury, and boiled out. The manometer, however, was not entirely satisfactory, as even after a second boiling out there remained a microscopic air bubble at the top of the tube. This appeared to increase somewhat during the course of the investigation. Repeated tests were made as to the possible effect of this source of error. Corrections were made for it where necessary. Finally the manometer was connected to a large bottle which served as a reservoir and this, in turn, was connected to an aspirator. A thermometer, hung beside the manometer, was of use in correcting the mercurial heights. The two arms of the manometer, which contained mercury, were of large and nearly equal bore, so that no correction for capillarity was necessary. The heights were read by means of a cathetometer about six feet distant, and sighted simultaneously on the manometer and on a steel tape suspended freely directly between the two limbs of the manometer. The tape naturally hung straight, but a small bob on the end also tended to ensure this. A Lufkin tape was selected which appeared to have very slight variations from the mean. It was then compared throughout its length with a standard meter at the temperature of the room, and a curve of corrections was constructed. Corrections for the expansion and contraction of the tape as the investigation proceeded were negligible, as were also corrections for the difference of level of the experimental tube and manometer, and for the latitude and altitude of Chicago.

It was necessary that the cross hairs of the cathetometer telescope should remain horizontal. This was ensured by giving the instrument a firm and level base and adjusting the wires by sighting at the edge of a level. This was tested repeatedly during the investigation.

The ethers investigated were methylpropyl, ethylpropyl, and dipropyl ether. As a control experiment, diethyl ether

was also purified and tested and values were obtained which were in harmony with those found by Ramsay and Young. The ethers were prepared according to the methods used by Thorpe and Rodger[1] in making the same ethers for viscosity determinations. They were dried for weeks over sodium wire and fractionally distilled with a Glinsky distilling head. Finally the observations were repeated for each of the substances, with different samples of the liquids, over part of the curve to confirm the results.

The corrected values of the vapor pressures are given in Tables VIII, IX, and X:

Table VIII.—*Vapor Pressure of Methylpropyl Ether.*

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
−0.60	15.18	21.01	38.83	31.87	59.40
3.42	18.00	23.00	42.05	32.72	61.25
7.01	21.26	23.91	43.60	33.80	63.39
8.81	23.09	24.85	45.33	34.84	65.81
12.58	27.22	26.80	48.75	35.58	67.52
14.30	29.33	28.25	51.76	36.73	70.38
18.67	35.26	29.06	53.34	38.34	73.95
17.60	33.69	30.12	55.59	39.34	76.56
20.02	37.60	31.01	57.45		

Table IX.—*Vapor Pressure of Ethylpropyl Ether.*

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
−1.02	4.98	26.40	18.80	56.23	59.06
−0.30	5.18	28.85	20.87	57.44	61.62
5.01	6.90	31.15	23.19	57.99	62.65
6.62	7.46	33.92	25.85	58.68	64.31
6.68	7.48	38.10	30.52	59.50	65.88
9.00	8.44	39.98	32.78	60.86	69.00
11.26	9.41	42.68	36.30	61.19	69.84
13.92	10.65	45.03	39.73	61.72	70.74
16.51	12.07	47.97	44.23	62.66	73.17
17.72	12.78	49.36	46.60	63.20	74.43
20.72	14.78	52.41	52.00	63.40	74.92
23.30	16.58	54.00	54.78	63.78	75.64
26.25	18.76	55.79	58.31		

[1] Phil. Trans., **189**, A, 103 (1897).

Table X.—*Vapor Pressure of Dipropyl Ether.*

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
8.80	2.99	45.23	15.50	77.40	51.76
11.95	3.42	49.53	18.49	79.00	54.69
18.40	4.73	57.50	25.51	80.40	57.21
21.42	5.54	59.70	27.84	81.80	59.80
24.05	6.21	62.47	30.98	83.19	62.50
27.61	7.37	66.30	35.62	84.75	65.46
28.71	7.69	70.01	40.41	86.10	68.24
33.01	9.54	71.99	43.26	86.89	70.14
41.60	13.41	73.60	45.66	88.78	74.11

These values were plotted on a large scale and the vapor pressures for every 10° read off from the curves. These values are given in Table XI, together with the corresponding fluidities. These last values were plotted against each other, as was done with the hydrocarbons, and the result is shown in Fig. II.

Table XI.—*The Corresponding Vapor Pressures and Fluidities of Ethers for Every 10° Centigrade.*

	Methylpropyl ether.		Ethylpropyl ether.		Dipropyl ether.		Diethyl ether.	
Temp.	p in mm.	φ.	p in mm.	φ.	p in mm.	φ.	p in mm. Ramsay and Young	φ.
0°	156.0	325.5	52.1	252.1	22.4	185.2	184.9	350.9
10°	242.6	361.0	88.5	282.5	31.8	210.3	291.78	387.2
20°	373.4	397.3	142.6	314.9	51.0	238.1	442.36	426.5
30°	552.5	437.0	219.5	349.0	82.0	266.7	647.92	467.3
40°	784.0	476.7	327.9	384.7	125.6	296.4	921.18	511.4
50°			476.7	422.1	189.6	328.2		
60°			670.2	462.5	281.8	360.9		
70°					404.2	395.9		
80°					563.6	432.6		
90°					776.0	472.5		

Fig. II shows that the fluidity-vapor pressure curves for ethers fall together into a single curve about as well as they do for the hydrocarbons, and the character of the curve is entirely similar, indicating again that *at high temperatures the fluidity is a linear function of the vapor pressure.* It is interesting to observe the possibility of predicting either the fluidity or the vapor pressure of any compound of these classes

of which either the vapor pressure or the fluidity, respectively, is known, or can be calculated. In fact, fluidities of compounds of these classes can be calculated, since they are unassociated. A word will be added on this point later in this paper.
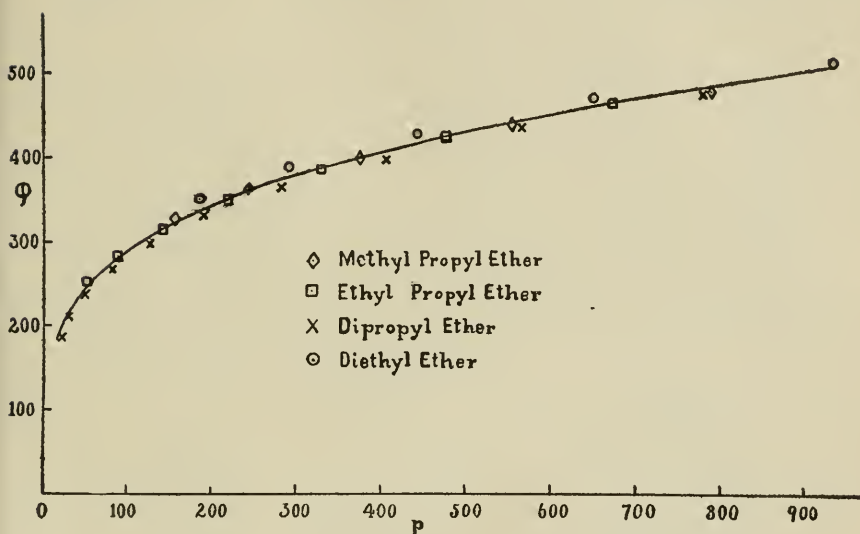
Figure II.—Fluidity-vapor pressure curve of the ethers.

Corresponding Condition.

Putting in other words the results of the examination of the fluidity-vapor pressure curves, I may state that *at temperatures corresponding to any given vapor pressure all aliphatic hydrocarbons and all ethers have nearly identical fluidities*, or, conversely, *at temperatures corresponding to any given fluidity the vapor pressures of these compounds are equal.* It was long ago observed that at temperatures of equal vapor pressure, particularly at the ordinary boiling point, substances are in a "corresponding condition." It is evident, therefore, at least for aliphatic hydrocarbons and ethers, that *when the liquids of a given class have equal fluidities, they are in a "corresponding condition."* It will be worth while to make a further investigation along this line with other classes of

unassociated compounds, as iodides and bromides. It is certain that associated compounds will give fluidity-vapor pressure curves which neither fall together in a single curve nor have any apparently simple relation to each other. To understand this would probably necessitate a knowledge of the cause of association and the laws governing it.

Temperature Coefficient of Association.

In a previous paper,[1] in calculating association, only the fluidity 200 was used for comparison, therefore it seemed desirable to make a comparison at some other fluidity in order to see how well different results agree by this method and also in order to obtain a temperature coefficient of association. For this purpose the fluidity 300 was selected. The following tables show how the constants were obtained:

Table XII.—*Value of a Methylene Grouping at the Fluidity* 300.

Substance.	Absolute temperature observed.	Difference.
Pentane	(258.2)	30.5
Hexane	288.7	24.4
Heptane	313.1	24.7
Octane	337.8	
Isopentane	(253.8)	29.2
Isohexane	283.0	22.3
Isoheptane	(305.3)	
Isoprene	(250.0)	24.4
Diallyl	274.4	
Methyl iodide	(338.5)	20.8
Ethyl iodide	(359.3)	23.2
Propyl iodide	(382.5)	
Isopropyl iodide	(371.6)	23.5
Isobutyl iodide	(595.1)	
Ethyl bromide	(311.5)	29.0
Propyl bromide	340.5	
Isopropyl bromide	(331.0)	26.8
Isobutyl bromide	357.8	
Isopropyl chloride	289.8	32.7
Isobutyl chloride	322.5	
Methylpropyl ether	265.5	22.9
Ethylpropyl ether	288.4	25.8
Dipropyl ether	314.2	
Methylisobutyl ether	284.9	19.6
Ethylisobutyl ether	304.5	

[1] Z. physik. Chem., **66**, 26 (1909).

If the mean of the above differences, 25.4, is taken as the value of a methylene grouping, it becomes possible to calculate the value of the hydrogen atom. First, however, it is important to find the value of the *iso* grouping:

Table XIII.—Value of the Iso Grouping at Fluidity 300.

Substance.	Normal position.	Iso	Difference.
Pentane	258.2	253.8	4.4
Hexane	288.7	283.0	5.7
Heptane	313.1	305.3	7.8
Propyl iodide	382.5	371.6	10.9
Propyl bromide	340.5	331.0	9.5
Propyl chloride	298.7	289.8	8.9
Butyric acid	426.5	416.7	9.8
Methyl butyrate	343.2	334.2	9.0

The value of the iso compound is on the average $8°.2$ lower than that of the normal compound.

Table XIV.—Value of Hydrogen at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. $n \times CH_2$	Difference.
Pentane	258.2	127.0	131.2
Hexane	288.7	152.4	136.3
Heptane	313.1	177.8	135.3
Octane	337.8	203.2	134.6
Isohexane	283.0	144.2	138.8
Isoheptane	305.3	169.6	135.7

This gives 135.6 as the value for H_2, 67.8 for H, and —110.2 for C.

The value of the double bond is obtained from the following table:

Table XV.—Value of the Double Bond at Fluidity 300.

Substance.	Normal.	Allyl.	Difference.
Iodide	382.5	380.5	2.0
Bromide	340.5	336.5	4.0
Chloride	298.7	291.9	6.8

It is seen that for a fluidity of 300, the value for an allyl compound is about $4°.3$ lower than for the normal compound,

which contains 2 atoms of hydrogen more. Therefore a double bond is equivalent to 131.3.

The value for oxygen is determined by means of the ethers:

Table XVI.—The Value of Oxygen at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. C_nH_{2n+2}.	Difference.
Methylpropyl ether	265.5	237.2	28.3
Ethylpropyl ether	288.4	262.6	25.8
Dipropyl ether	314.2	288.0	26.2
Methylisobutyl ether	284.9	254.4	30.5
Ethylisobutyl ether	304.5	279.8	24.7
		Average,	27.1

For the determination of association in aromatic compounds it is necessary to get the value of the ring grouping, if, as in our preceding paper, we assume the benzene formula of Kekulé with 3 double bonds. This is done in Table XVII.

Table XVII.—Value of the Benzene Ring at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. C_nH_{2n-6}.	Difference.
Benzene	348.1	139.5	208.6
Toluene	347.5	164.9	182.6
Ethylbenzene	362.1	190.3	171.8
o-Xylene	377.5	190.3	176.2
m-Xylene	355.5	190.3	164.2
p-Xylene	357.4	190.3	167.1

The differences vary widely from each other. If, as before, it is assumed that this is due to unlike association in these hydrocarbons, then we may take the smallest value, *viz.*, 164.2, as the maximum value of the constant. Since *m*-xylene may be somewhat associated, it is evident that associations calculated with this constant are minimum values. Hence, where this constant is used the association will be marked with a + sign.

In Table XVIII I have grouped together for comparison the constants at fluidities 200 and 300:

Table XVIII.—Constants at Fluidity 200 and Fluidity 300.

Atom or grouping.	$\varphi = 200.$	$\varphi = 300.$	Atom or grouping.	$\varphi = 200.$	$\varphi = 300.$
Carbon	—95.7	—110.2	Iso	—7.6	—8.2
Hydrogen	59.2	67.8	Double bond	114.4	131.3
Oxygen	24.2	27.1	Benzene ring	141.8	164.2

Using these constants, the temperatures corresponding to a fluidity of 300 were calculated for a large number of associated compounds. The observed temperatures are invariably higher than the temperatures calculated from the constants derived from unassociated compounds. Since the values of the constants are additive, it is evident that the association is obtained by simply dividing the observed by the calculated values. From the associations at fluidities 200 and 300 and the temperatures corresponding to these fluidities the temperature coefficient of association, *i. e.*, the mean decrease in the association (between the temperature limits indicated) for a rise in temperature of 1° C., is calculated. These results are given in Table XIX. Column 2 gives the observed temperatures corresponding to a fluidity of 300, column 3 the calculated temperature, and column 4 the association for that fluidity. Column 5 gives the association already calculated for a fluidity of 200 and column 6 the temperature coefficient of association.

The results are perhaps most noteworthy in the close agreement between the association at the two fluidities. Usually the decrease in association as the temperature is raised is very small, but it is considerable in water and the alcohols, and this is true in spite of the fact that some other substances are even more highly associated. Thus, acetic acid is highly associated, but the temperature coefficient of association is much smaller than that for amyl alcohol, which is very much less associated over the range of temperature studied. Evidently amyl alcohol is very highly associated at low temperatures. All of these facts are in harmony with conclusions already drawn from a study of the fluidity curves over a large temperature range.[1]

[1] Z. physik. Chem., **66,** 7 *et seq.* (1909).

Table XIX.—*Temperature Coefficients of Association.*

Substance.	Temperature observed. $\varphi = 300$.	Temperature calculated. $\varphi = 300$.	Association. $\varphi = 300$.	Association. $\varphi = 200$.	Temperature coefficient.
Water	358.5	162.7	2.20	2.31	0.0038
Dimethyl ketone	289.5	207.5	1.23	1.23	0.000
Diethyl ketone	326.5	285.4	1.14	1.14	0.000
Methylethyl ketone	315.6	260.0	1.21	1.22	0.000
Methylpropyl ketone	330.0	285.4	1.17	1.16	0.000
Acetic acid	407.9	236.3	1.73	1.77	0.001
Propionic acid	408.5	261.7	1.55	1.57	0.001
Butyric acid	426.5	287.1	1.48	1.51	0.001
Isobutyric acid	416.7	278.9	1.49	1.51	0.001
Acetic anhydride	388.1	309.9	1.25	1.25	0.000
Propionic anhydride	402.4	360.7	1.11	1.12	0.000
Benzene	348.1	303.7	1.14+	1.17+	0.001
Toluene	347.5	329.1	1.06+	1.06+	0.000
Ethylbenzene	362.1	354.5	1.02+	1.02+	0.000
o-Xylene	377.5	354.5	1.06+	1.07+	0.000
m-Xylene	355.5	354.5	1.00+	1.00+	0.000
p-Xylene	357.4	354.5	1.00+	1.00+	0.000
Methyl alcohol	336.9	188.1	1.79	1.84	0.002
Ethyl alcohol	(371.5)	213.5	(1.74)	1.83	0.003
Active amyl alcohol	(408.7)	289.7	(1.41)	1.54	0.005
Inactive amyl alcohol	(415.5)	289.7	(1.30)	1.55	0.008
Allyl alcohol	378.7	234.6	1.61	1.69	0.003
Methyl formate	297.5	236.3	1.26	(1.25)	0.000
Ethyl formate	311.4	261.7	1.19	1.19	0.000
Propyl formate	333.9	287.1	1.16	1.17	0.000
Methyl acetate	306.0	261.7	1.17	(1.17)	0.000
Ethyl acetate	320.8	287.1	1.12	1.12	0.000
Propyl acetate	343.0	312.5	1.09	1.11	0.001

It may be noted here that it is possible to calculate the general fluidity equation of an unknown substance. The slopes of the fluidity curves of a number of classes of compounds for a fluidity of 200[1] and the constants for fluidities 200 and 300 have been given. Since the slope in a given class remains constant and the absolute temperature corresponding to fluidities of 200 and 300 can be calculated, the constants in the equation $t = A\varphi - \dfrac{B}{\varphi} + C$ may be found.

[1] Z. physik. Chem., **66**, 27 *et seq.* (1909).

Having found the fluidity curve, it becomes theoretically possible to calculate the vapor pressure curve, as already pointed out.

The Kekulé Formula for Benzene.

I have shown that oxygen has the same value in all compounds, whereas viscosity workers have heretofore found it necessary to give oxygen different values in the different classes of compounds. I have regarded this as a strong evidence in favor of the correctness of my hypothesis that fluidities, and not viscosities, are additive. But it was necessary to assume a value for a benzene grouping, as did also Thorpe and Rodger, when I started out on the hypothesis that benzene contained 3 double bonds according to the Kekulé formula. But there is another way of regarding the matter. For C_6H_6 differs from the corresponding aliphatic hydrocarbon C_6H_{14} by 8 hydrogen atoms. Now we have seen that 2 hydrogen atoms equal 135.6 at a fluidity of 300. And without any hypothesis as to what a "double bond" may be, we have the fact that an allyl compound contains 2 hydrogen atoms less than the corresponding saturated compound, yet the temperature is only 4°.3 lower than for the saturated compound at the same fluidity of 300. Hence we may say that the compound compensates in some way for the loss of the 2 hydrogen atoms to the extent of 131.3, but since benzene has 8 less hydrogen atoms than the saturated compound, the simplest assumption is that the loss will be compensated for to the extent of $4 \times 131.3 = 525.2$. Recalculating the association of the aromatic hydrocarbon on this assumption, we obtain the following table:

Table XX.—Association of Aromatic Hydrocarbons at Fluidity 300 without Assuming the Kekulé Formula for Benzene with Three Double Bonds.

Substance.	Temperature observed.	Temperature calculated. $C_nH_{2n} - 6$.	Association.
Benzene	348.1	270.8	1.29
Toluene	347.5	296.2	1.17
Ethylbenzene	362.1	321.6	1.13
o-Xylene	377.5	321.6	1.17
m-Xylene	355.5	321.6	1.11
p-Xylene	357.4	321.6	1.11

The values calculated earlier were admittedly minimum values. These values therefore have a certain advantage. It is impossible to affirm at this stage of the work that the ring grouping does not have a value, hence these may be maximum values. These values are in fact somewhat higher than the values for these substances determined by other workers.

Association in Mixtures.

Having found it possible to calculate the association of pure liquids with success by making use of the fluidity data, it seemed advisable to investigate liquid mixtures with the hope of learning something as to their condition in regard to chemical combination or association. In getting the association of liquids a certain fluidity was chosen and the temperatures calculated at which each liquid should have this fluidity. Unfortunately, the viscosities of liquid mixtures have been measured at only a few temperatures at the most, hence the comparison at a given fluidity cannot be made without much new experimental work on these mixtures. I have tried to work out a method of comparison at a given temperature, but while some interesting relations were brought out, assumptions seemed necessary which destroy the usefulness of the method. Of course there is also a theoretical objection to making a comparison at constant temperature, since the substances would be very far from being in a "corsponding condition" as is the case when the temperatures of equal fluidities are compared. My next work will therefore be to measure the viscosities of a series of mixtures over a range of temperature.

CONCLUSIONS.

1. A summary has been given of the evidence accumulated thus far to prove that fluidities and not viscosities are additive.

2. Attention was called to the identity of the equation proposed in 1906 with the equation derived in 1909, tested and proved satisfactory for a large number of substances.

3. The possibility of a connection between volume and

fluidity was noted. Van der Waal's equation in terms of volume, when the pressure is constant, is very similar to my simple equation. Moreover, on substituting fluidity in place of volume this equation reproduces fluidity (or viscosity) data with greater fidelity than any equation heretofore proposed except my modified equation.

4. A careful examination of the fluidity curve of water in the region of 4° indicates a sagging of the curve coincident with the minimum in volume.

5. Since the fluidity of liquids increases with the temperature, and the fluidity of gases decreases with the temperature, there must be a maximum in fluidity and it is proposed to investigate whether or not this lies at the critical point.

6. Since it was observed that the fluidities of all aliphatic hydrocarbons and all ethers are nearly identical at their boiling points, it seemed desirable to learn whether or not this relation between fluidity and vapor pressure was general. The data at hand have proved it to be so for the hydrocarbons.

7. Measurements of the vapor pressures of methylpropyl ether, ethylpropyl ether, and dipropyl ether were made between 0° C. and their boiling points. The relation between fluidity and vapor pressure at their boiling points was also found to be general in the case of the ethers.

8. Furthermore, it appears to be true that at high temperatures the fluidity is a linear function of the vapor pressure.

9. Evidence has been given to prove that at temperatures of equal fluidity substances are in corresponding condition.

10. The "constants" corresponding to a fluidity of 300 have been given and the association of a number of substances calculated. From these values and those obtained previously the temperature coefficients of association have been calculated. In spite of using different substances for calculating the constants, the values of the association at the different fluidities are entirely harmonious.

11. Future work on liquid mixtures has been outlined.

RICHMOND COLLEGE,
   RICHMOND, VA.,
     JAN. 12, 1910.

CLXXVIII.—RESEARCHES ON AMINES: SYNTHESES OF 4-NITROPHENYLETHYLAMINE AND 2,4-DINITROPHENYLETHYLAMINE.

[SECOND PAPER.]

By Treat B. Johnson and Herbert H. Guest.

The three possible mononitrobenzylamines[1] (*o*,- *m*- and *p*-) have been synthesized, but no nitro derivatives of the simplest β-amine of the aromatic series, phenylethylamine, I, are described in Beilstein's *Handbuch*. It was therefore of interest, in our study of β-amines and their substitution products, to investigate the nitro derivatives of this base. We describe in this paper, the preparation and properties of *p*-nitrophenylethylamine, III, 2,4-dinitrophenylethylamine, IV, and incidentally several derivatives of these two bases and also of *o*-nitrophenylethylamine, II.

| $CH_2CH_2NH_2$ | $CH_2CH_2NH_2$ | $CH_2CH_2NH_2$ | $CH_2CH_2NH_2$ |
| I. | II. | III. | IV. |
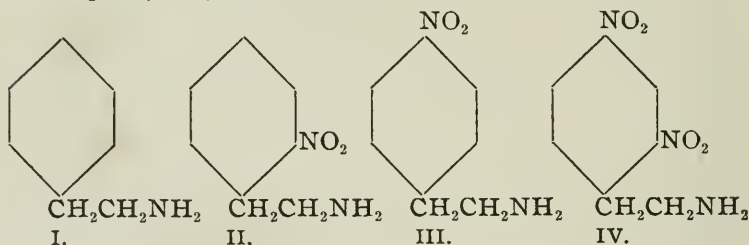
It is a well-known fact that, in the nitration of acetanilide, the acetyl group favors substitution in the *para* position. This amide reacts with nitric acid, giving an excellent yield of *p*-nitroacetanilide[2] (95 per cent. of the theoretical), while benzanilide gives a mixture of the three mononitro derivatives (*o*-, *m*- and *p*-), in which the *ortho* and *para* compounds are present in about equal proportions.[3] Acetylbenzylamine[4] also reacts with nitric acid, giving chiefly acetyl-*p*-nitro-

[1] Gabriel: Ber. d. chem. Ges., **20**, 2228. Gabriel and Hendess: *Ibid.*, **20**, 2869. Gabriel and Jansen: *Ibid.*, **24**, 3092. Hafner: *Ibid.*, **23**, 338.

[2] Nölting and Collins: *Ibid.*, **17**, 262.

[3] Hübner: Ann. Chem. (Liebig), **208**, 292.

[4] Strakosch: Ber. d. chem. Ges., **5**, 697. Rudolph: *Ibid.*, **12**, 1297.

benzylamine.[1] These observations suggested that the introduction of a nitro group into the *para* position in phenylethylamine would be effected smoothly by nitration of acetylphenylethylamine.[2] The results of our experiments confirmed this assumption.

Acetylphenylethylamine, VII, was prepared for our work by acetylation of phenylethylamine with thioacetic acid. We now find that this amide reacts smoothly with nitric acid (sp. gr. 1.51) below 5°, giving a mixture of the *ortho-* and *paranitro* acetyl derivatives, X and XI. The *para* compound, however, is the chief product of the reaction, under these conditions, and the yield corresponds to about 70 per cent. of the theoretical. The formation of a dinitro derivative was not observed. Acetyl-2,4-dinitrophenylethylamine, VIII, however, is obtained when acetylphenylethylamine is nitrated in the presence of concentrated sulphuric acid. The structures of this dinitro compound, VIII, and of acetyl-*p*-nitrophenylethylamine, XI, were established by the facts that they were converted into 2,4-dinitrobenzoic[3] and *p*-nitrobenzoic[4] acids, respectively, by oxidation with potassium dichromate and sulphuric acid. The nitrophenylethylamines, XIII, XII, and IX, are formed quantitatively by hydrolysis of their corresponding acetyl derivatives with hydrochloric and hydrobromic acids.

Especially interesting was the action of nitric acid (sp. gr. 1.51) on phthalylphenylethylamine, V, under the same conditions as are favorable for the formation of a mononitro derivative from acetylphenylethylamine. The chief product of the reaction, in this case, was phthalyl-2,4-dinitrophenylethylamine, VI, and it was with some difficulty that we were able to isolate a mononitro derivative sufficiently pure for analysis. The structure of this dinitro compound, VI, was determined by the fact that it gave, on hydrolysis, the same

[1] Amsel and Hofmann: Ber. d. chem. Ges., **19,** 1286.

[2] Bischler and Napieralski: Ber. d. chem. Ges., **26,** 1905. Michaelis and Simon: *Ibid.,* **26,** 2167.

[3] Tiemann and Judson: Ber. d. chem. Ges., **3,** 223. Griess: *Ibid.,* **7,** 1225. Hübner: Ann. Chem. (Liebig), **222,** 79.

[4] Beilstein and Wilbrand: Ann. Chem. (Liebig), **128,** 257. Beilstein and Geitner: *Ibid.,* **139,** 335.

$$C_6H_5CH_2CH_2CH_2N(CO)_2C_6H_4 \longrightarrow \overset{2.4.}{(NO_2)_2}\overset{1}{C_6H_3}CH_2CH_2CH_2N(CO)_2C_6H_4$$

$$V. \qquad\qquad VI.$$

$$\overset{2.4.}{(NO_2)_2}\overset{1}{C_6H_3}CH_2CH_2CH_2NHCOCH_3 \longrightarrow \overset{2.4.}{(NO_2)_2}\overset{1}{C_6H_3}CH_2CH_2CH_2NH_2$$

$$VIII. \qquad\qquad IX.$$

$$\overset{2}{C_6H_5}.CH_2CH_2CH_2NHCOCH_3$$

$$VII.$$

$$\overset{2}{NO_2}.\overset{1}{C_6H_4}.CH_2CH_2CH_2NHCOCH_3 \qquad \overset{4}{NO_2}.\overset{1}{C_6H_4}.CH_2CH_2CH_2NHCOCH_3 \longrightarrow \overset{4}{NO_2}.\overset{1}{C_6H_4}CH_2CH_2CH_2NH_2$$

$$X. \qquad\qquad XI. \qquad\qquad XII.$$

$$\overset{2}{NO_2}C_6H_4.\overset{1}{C}H_2CH_2CH_2NH_2 \qquad \overset{4}{NH_2}.\overset{1}{C_6H_4}CH_2CH_2CH_2NHCOCH_3 \longrightarrow \overset{4}{NH_2}.\overset{1}{C_6H_4}CH_2CH_2CH_2NH_2$$

$$XIII. \qquad\qquad XIV. \qquad\qquad XV.$$

dinitrophenylethylamine, IX, as was obtained by hydrolysis of acetyl-2,4-dinitrophenylethylamine, VIII.

The acetyl derivatives of *ortho*- and *para*nitrophenylethyl-amines and also of 2,4-dinitrophenylethylamine are weak bases, whose salts undergo dissociation in water. Acetyl-*o*-nitrophenylethylamine, X, is apparently more basic than the isomeric *para* compound, XI. Acetyl-*p*-nitrophenylethyl-amine is converted quantitatively into acetyl-*p*-aminophenyl-ethylamine, XIV, by reduction with aluminium amalgam. This is a strong diacid base and forms a stable dihydrochlor-ide. On the other hand, when reduced with tin and hydro-chloric acid the amide underwent hydrolysis, with loss of the acetyl group, giving *p*-aminophenylethylamine, XV. This behavior is perfectly analogous to that of acetyl-*p*-nitro-benzylamine, under the same conditions, which is converted smoothly into *p*-aminobenzylamine.[1]

An attempt to synthesize *p*-aminophenylethylamine, XV, by reduction of *p*-aminobenzyl cyanide[2] with sodium and alco-hol was unsuccessful. This nitrile, to our surprise, was re-duced abnormally, giving an excellent yield of *p*-toluidine. Other alkyl nitriles, it has been observed, are reduced in this abnormal manner. Toluene is invariably formed, as a by-product, in the reduction of benzyl cyanide with sodium and alcohol. Bamberger and Immerwahr[3] observed that diphenylacetonitrile is reduced, under these conditions, giv-ing a mixture of diphenylmethane and *unsymmetrical* diphenyl-ethylamine. It is of interest to note also, in this connection, that one reason for a small yield of *p*-hydroxyphenylethyl-amine, by reduction of *p*-hydroxybenzyl cyanide with sodium and alcohol,[4] is that part of the nitrile is reduced abnor-mally, giving *p*-cresol.

After the completion of the work described in this paper a publication by Barger and Walpole[5] appeared, in which they describe the action of fuming nitric acid on benzoylphenyl-

[1] Ber. d. chem. Ges., **19**, 1286.
[2] Pschorr, Wolfes and Buchow: *Ibid.*, **33**, 162.
[3] *Ibid.*, **33**, 2845.
[4] Barger: J. Chem. Soc., **95**, 1123 (1909).
[5] *Ibid.*, **95**, 1720.

ethylamine and acetylphenylethylamine. They observed that substitution took place in the *para* positions and obtained a yield of benzoyl-*p*-nitrophenylethylamine corresponding to only 35 per cent. of the calculated amount. The results obtained by nitration of the acetylphenylethylamine were less satisfactory and the yield of *p*-nitro compound is not given. The corresponding *ortho* derivatives were not isolated.

EXPERIMENTAL PART.

Acetylphenylethylamine, $C_6H_5CH_2CH_2NHCOCH_3$.—We prepared this amide[1] by acetylation of phenylethylamine with thioacetic acid. Fifty-three grams of the freshly distilled amine were placed in a dry flask, connected with a reflux condenser, and 40 grams of thioacetic acid (1 mol. = 33.3 grams) then added slowly to the amine through the condenser tube. There was an immediate reaction with evolution of heat and formation of hydrogen sulphide. After addition of the thio acid the mixture was heated in an oil bath at 210°–220° for 1 hour and finally for a few minutes, at 290°, in a sand bath to remove the excess of thioacetic acid. On cooling, the amide completely solidified and was used for our experiments without further purification. The yield was 70 grams, or 98 per cent. of the theoretical.

*Acetyl-*p-*nitrophenylethylamine*,
$(p)NO_2C_6H_4CH_2CH_2NHCOCH_3$.—An excellent yield of this amide is easily obtained by nitration of acetylphenylethylamine under the following conditions: Thirty-five cc. of nitric acid (sp. gr. 1.51) are cooled to 0° and 10 grams of the amide added slowly. The amide dissolves immediately with evolution of heat and in order to obtain the best results it is advisable not to allow the temperature of the solution to rise above 5°. After allowing to stand for 10–15 minutes the acid solution is diluted with ice water until it assumes a turbid appearance and the nitric acid then neutralized, at a low temperature, with ammonia. The amide separates in prismatic crystals which usually melt at 130°–140°. After nitration of 70 grams of acetylphenylethylamine, under these

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[1] Bischler and Napieralski: *Loc. cit.* Michaelis and Simon: *Loc. cit.*

conditions, 55 grams of the *p*-nitro compound, correspond-
ing to about 62 per cent. of the theoretical yield, separated
after neutralization with ammonia. The amide is very soluble
in hot and moderately soluble in cold alcohol. It is soluble
in boiling water, but separates on cooling as an oil, which soon
crystallizes in colorless, prismatic crystals melting at 141°–
142° if heated rapidly. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{12}O_3N_2$.	Found.	
		I.	II.
N	13.46	13.5	13.7

In order to isolate the other products of this reaction the
ammoniacal filtrate, after filtering off the acetyl-*p*-nitro-
phenylethylamine, was concentrated on the steam bath,
until ammonium nitrate began to separate, and cooled. We
obtained about 15 grams of crystalline material which proved
to be a mixture of acetyl-*p*-nitrophenylethylamine and the
isomeric *ortho* derivative melting from 90°–120°. They
were easily separated by trituration with cold dilute hydro-
chloric acid, in which the *ortho* compound is very soluble (see
below). The insoluble *para* compound was then dried on a
porous plate and recrystallized once from 95 per cent. alcohol.
We recovered in this manner 3.5 grams melting at 135°–
137.°

Acetyl-o-*nitrophenylethylamine*,
$(o)NO_2C_6H_4CH_2CH_2NHCOCH_3$.—When the hydrochloric acid
solution above was neutralized with ammonia this compound
separated as an oil which solidified when cooled at 0°. It
was then dried on a porous plate to free it from oil and puri-
fied by repeated crystallizations from dilute alcohol and ben-
zene. It was easily soluble in boiling benzene but separated
on cooling in slender prisms melting at 86°–88° to a clear
oil. Analysis (Kjeldahl):

| | Calculated for $C_{10}H_{12}O_3N_2$. | Found. |
| N | 13.4 | 13.11 |

This amide undergoes hydrolysis when digested with hydro-
bromic acid, giving the hydrobromide of o-*nitrophenylethyl-*

amine. The free base separated as an oil, heavier than water, when the salt was decomposed by alkali, and gave a crystalline picrate, which was soluble in alcohol and melted at 147° to an oil.

Oxidation of Acetyl-p-nitrophenylethylamine with Potassium Dichromate.—Seventh-tenths gram of the nitro compound was oxidized for 1.5 hours at 100° with 2.5 grams of potassium dichromate, dissolved in a mixture of 5 cc. of concentrated sulphuric acid and 15 cc. of water. The solution assumed a green color and prismatic crystals slowly deposited from the hot solution. After cooling, they were separated by filtration and purified by crystallization from hot water. The substance melted at 237°–238° and was identified as *p*-nitrobenzoic acid.[1] A mixture of this oxidation product and the pure *p*-nitro acid melted at the same temperature. Analysis (Kjeldahl):

	Calculated for $C_7H_5O_4N$.	Found.
N	8.38	8.37

Hydrochloride of Acetyl-p-nitrophenylethylamine,
$(p)NO_2C_6H_4CH_2CH_2NHCOCH_3.HCl.$—The amide is a weak base and dissolves in concentrated hydrochloric acid, giving a stable salt which can be digested with hydrochloric acid for hours without change. One gram was dissolved in 20 cc. of boiling acid and the solution cooled, when the hydrochloride separated in prisms, melting at 179°–180°, with effervescence, to a dark oil. It is very soluble in cold, absolute alcohol and dissociates in water, giving the free amide melting at 141°–142°. Analysis:

0.1064 gram substance gave 0.0613 gram AgCl.

	Calculated for $C_{10}H_{12}O_3N_2.HCl.$	Found.
Cl	14.51	14.24

p - *Aminophenylethylamine,* $(p)NH_2C_6H_4CH_2CH_2NH_2.$ — A quantitative yield of the hydrochloride of this base can be obtained by reduction of acetyl-*p*-nitrophenylethylamine with tin and hydrochloric acid. One gram of the amide was dis-

[1] *Loc. cit.*

solved in a mixture of 10 cc. of 95 per cent. alcohol and 10 cc. of concentrated hydrochloric acid and reduced with an excess of tin for 2.5 hours at 55°–58°. The excess of hydrochloric acid was then removed by evaporation at 100°, the tin salt dissolved in cold water and the tin precipitated as sulphide with hydrogen sulphide. When this solution was concentrated we obtained a crystalline hydrochloride, which was identified as a salt of *p*-aminophenylethylamine. It was extremely soluble in cold water and was purified for analysis by crystallization from a mixture of alcohol and ether. It separated as a granular powder which had no definite melting point but decomposed from 270°–280°, according to the rate of heating. The base separates as an oil when the salt is treated with alkali. Analysis:

0.1267 gram substance gave 0.1611 gram AgCl.

	Calculated for		Found.
	$C_8H_{14}N_2Cl_2$.	$C_8H_{14}N_2Cl_2.H_2O$.	
Cl	33.48	31.27	31.45

Platinum Salt.—This was prepared by adding hydrochlorplatinic acid to an alcoholic solution of the hydrochloride. It separated in clusters of sharp-edged prisms which had no definite melting point. Analysis:

	Calculated for $(C_8H_{14}N_2Cl_2)_2.2PtCl_4$.	Found.
Pt	35.6	35.1

Picrate.—Crystallizes from hot water in needlelike prisms which melt at 223°–224° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_8H_{14}N_2Cl_2(C_6H_2O_7N_3)_2$.	Found.
N	18.91	18.90
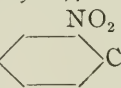
*Acetyl-*p-*aminophenylethylamine,*
(*p*)$NH_2C_6H_4CH_2CH_2NHCOCH_3$.—A quantitative yield of this base is obtained by reduction of the corresponding nitro derivative, in dilute alcohol, with aluminium amalgam. After filtration from the aluminium hydroxide and evaporation of the alcohol the base was obtained as a thick syrup, which did

not solidify after standing at ordinary temperature for 10 hours. It dissolved in hydrochloric acid, giving a hygroscopic dihydrochloride, which was extremely soluble in water and absolute alcohol. It crystallizes from a hot, saturated, aqueous solution in clusters of radiating prisms. When heated in a capillary tube the salt sintered above 170° and decomposed at 191°–192° with violent effervescence. The salt was dried for analysis in a desiccator over concentrated sulphuric acid and potassium hydroxide. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{14}ON_2(HCl)_2$.	Found.
N	11.1	10.91

Acetyl-2,4 dinitrophenylethylamine,

$$NO_2\underset{NO_2}{\overset{NO_2}{\bigcirc}}CH_2CH_2NHCOCH_3.$$—A good yield of this compound is obtained by dissolving 2.0 grams of acetylphenylethylamine or acetyl-p-nitrophenylethylamine in a mixture of 6 cc. of concentrated sulphuric and nitric (sp. gr. 1.51) acids. After allowing to stand for a few minutes *only* at 10°–20° the acid solution is then diluted with ice water and neutralized at a low temperature with ammonia. The dinitro derivative separates as a yellow oil which soon crystallizes. It is extremely soluble in alcohol and moderately soluble in boiling water. It was purified for analysis by recrystallization from hot water and separated, on cooling, as an oil which soon crystallized in characteristic prisms melting at 97°–98° to a yellow oil with no effervescence. The compound is basic and dissolves at once in dilute hydrochloric acid. Analysis (Kjeldahl):

	Calculated for		Found.
	$C_{12}H_{11}O_5N_3$.	$C_8H_9O_4N_3$.	
N	16.60	19.90	16.68

Oxidation of Acetyl-2,4-dinitrophenylethylamine with Potassium Dichromate.—Nine-tenths of a gram of the dinitro compound was dissolved in a solution of 3.2 grams of potassium dichromate in 6.5 cc. of concentrated sulphuric acid and heated for 12 hours at 100°. On cooling, a crystalline substance

separated, which was purified by crystallization from hot water. It separated on cooling in long, yellow needles melting at 177°–179°. The compound was soluble in alkalis and was identified as 2,4-dinitrobenzoic acid.[1] A mixture of the oxidation product and Kahlbaum's 2,4-dinitrobenzoic acid melted sharply at 180°.

Phthalylphenylethylamine, $C_6H_5CH_2CH_2N(CO)_2C_6H_4$, was prepared by carefully mixing 15 grams of phenylethylamine with the calculated amount of finely pulverized phthalic anhydride (20 grams) and heating in an oil bath at 140°–150° for about 2 hours. It crystallizes from boiling alcohol in well-developed prisms or tables which melt at 133°. The yield of pure amide was 26 grams. Analysis (Kjeldahl):

	Calculated for $C_{16}H_{13}O_2N$.	Found.
N	5.57	5.30

Phthalyl-2,4-dinitrophenylethylamine,

$$NO_2 \langle\! \overset{NO_2}{} \rangle CH_2CH_2N(CO)_2C_6H_4.$$—Five grams of phthalyl-phenylethylamine were dissolved in 20 cc. of nitric acid (sp. gr. 1.51), cooled below 10°, and the mixture allowed to stand for 30 minutes. It was then poured upon crushed ice when the dinitro compound separated in colorless, prismatic crystals. The amide is insoluble in water and alcohol, but soluble in boiling glacial acetic acid, from which it separates, on cooling, in rhombic tables melting at 215°. The weight of the crude dinitro compound was 4.5 grams, corresponding to 70 per cent. of the theoretical yield. Analysis (Kjeldahl):

	Calculated for		Found.
	$C_{16}H_{12}O_4N_2$.	$C_{16}H_{11}O_6N_3$.	
N	9.46	12.2	11.8

When the acid filtrate above was concentrated we obtained a crystalline product which crystallized from glacial acetic acid in needles melting at 170°–176°. This substance was apparently a mixture of the dinitro and mononitro amides

[1] *Loc. cit.*

and melted after several recrystallizations from alcohol and acetic acid at 178°–180°. A nitrogen determination (Kjeldahl) gave 10.3 per cent., while the calculated value for a mononitro compound is 9.46 per cent. It was not investigated further.

p-*Nitrophenylethylamine*, $(p)NO_2C_6H_4CH_2CH_2NH_2$. — This amine was obtained in the form of its hydrobromide and hydrochloride by hydrolysis of acetyl-*p*-nitrophenylethylamine with hydrobromic and hydrochloric acids, respectively. Forty-two grams of the acetyl compound were dissolved in 70 cc. of hydrobromic acid (sp. gr. 1.48) and the solution heated to boiling, in an oil bath, for 3 hours. When the excess of hydrobromic acid was removed by evaporation, we obtained 46 grams of the hydrobromide, or 92.5 per cent. of the theoretical yield. This salt is very soluble in water and crystallizes from boiling 95 per cent. alcohol in plates, which melt at 218°–219° to a dark oil. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_2N_2.HBr.$	Found.
N	11.33	11.6

A theoretical yield of the *hydrochloride* was obtained by heating the amide with concentrated hydrochloric acid at 140°–150°. This salt is extremely soluble in water. It was purified for analysis by crystallization from absolute alcohol and separated, on cooling, in characteristic, tabular crystals or prisms which melted at 212°–214° to a clear oil with violent effervescence. Analysis:

0.1552 gram substance gave 0.1120 gram AgCl.

	Calculated for $C_8H_{10}O_2N_2.HCl.$	Found.
Cl	17.52	17.7

p-*Nitrophenylethylamine* separated as a yellow oil when its salts were decomposed by alkali. It is a strong base which absorbs carbon dioxide from the air, giving a crystalline carbonate. The base cannot be distilled with steam. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_2N_2.$	Found.
N	16.86	16.5

Platinum Salt.—This crystallizes from hot water in prismatic crystals, which decompose at 223°.

1-Phenyl-2-(p-*Nitrophenylethyl*)*thiourea*,
$C_6H_5NHCSNHCH_2CH_2C_6H_4NO_2(p)$.—From phenyl isothiocyanate and *p*-nitrophenylethylamine. It crystallizes from alcohol in stout prisms which melt at 136° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{15}O_2N_3S$.	Found.
N	13.95	13.70

Benzenesulphone-p-*nitrophenylethylamine*,
~~$C_6H_5SO_2NHCH_2CH_2C_6H_4NO_2(p)$~~.—This was prepared by the action of benzenesulphone chloride on *p*-nitrophenylethylamine in presence of sodium hydroxide. It is soluble in warm sodium hydroxide solution, giving a sodium salt which crystallizes, on cooling, in plates. The amide is soluble in benzene and insoluble in water. It crystallizes from alcohol in prisms which melt at 107°–108°. Nitrogen determinations on the air-dried material indicated that the amide contained alcohol of crystallization (Kjeldahl):

	Calculated for		Found.	
	$C_{14}H_{14}O_4N_2S$.	$C_{14}H_{14}O_4N_2S.C_2H_5OH$.	I.	II.
N	9.15	7.9	7.75	7.53

Benzenesulphonemethyl-p-*nitrophenylethylamine*,
$C_6H_5SO_2N(CH_3)CH_2CH_2C_6H_4NO_2(p)$.—Ten grams of benzenesulphone-*p*-nitrophenylethylamine and 1 gram of sodium hydroxide were dissolved in 75 cc. of alcohol and 7 grams of methyl iodide added to the solution. After heating on the steam bath for 4 hours, the alcohol was evaporated and the product obtained triturated with cold water to remove sodium iodide. The amide was insoluble in water but soluble in boiling alcohol. It separated, on cooling, in rectangular crystals which melted at 98° to an oil. A mixture of this compound and benzenesulphone-*p*-nitrophenylethylamine melted at 74°–98°. The yield was 9 grams. The compound was insoluble in sodium hydroxide solution. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{16}O_4N_2S$.	Found.
N	8.7	8.30

2,4-Dinitrophenylethylamine, $NO_2\overbrace{}^{NO_2}CH_2CH_2NH_2$.—The hydrochloride of this base is obtained by hydrolysis of acetyl-2,4-dinitrophenylethylamine, or the corresponding phthalyl compound, with hydrochloric acid, at 140°–150°. It is very soluble in water and moderately soluble in cold alcohol. It crystallizes from absolute alcohol in prisms which melt at 197°–198° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_4N_3Cl$.	Found.
N	16.97	16.89

The free base is precipitated as a heavy oil when sodium hydroxide is added to an aqueous solution of the hydrochloride.

Picrate.—Crystallizes from hot water in needles which melt at 159° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{12}O_{11}N_6$.	Found.
N	19.0	18.80

1-Phenyl-2-(2,4-dinitrophenylethyl)thiourea,

$C_6H_5NHCSNHCH_2CH_2\overbrace{}^{NO_2}NO_2$.—Crystallizes from alcohol in plates which melt at 128°. It is difficultly soluble in benzene. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{14}O_4N_4S$.	Found.
N	16.1	15.75

New Haven, Conn.,
January 1, 1910.

ON THE APPLICATION OF PHYSICAL-CHEMICAL METHODS TO DETERMINE THE MECHANISM OF ORGANIC REACTIONS.

By Arthur Michael.

S. F. Acree and his coworkers have published a number of interesting investigations on phenylurazole and its deriva-

tives, from the experimental results of which the former chemist has drawn the following conclusions regarding the mechanism of tautomeric reactions:

"A salt of a tautomeric compound reacts with an alkyl halide, or other reagent, and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions."[1] Thus the sodium derivative of 4-methylphenylurazole exists in solution as

$$C_6H_5-N\overline{\quad\quad}N\,Na \qquad\qquad C_6H_5N\overline{\quad\quad}N$$

$$OC \qquad CO \qquad\qquad\qquad OC \qquad CONa\,.$$

$$NCH_3 \qquad\qquad\qquad\qquad NCH_3$$

$$\text{A.} \qquad\qquad\qquad\qquad\qquad \text{B.}$$
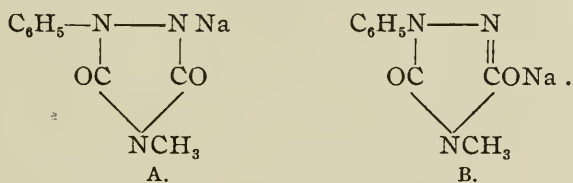
When an alkyl halide, or other organic reagent, reacts on such tautomeric salts in solution the reaction takes place practically completely between the anions of the two salts and the halide.[2]

On the basis of these generalizations, Acree discusses the several hypotheses which have been previously advanced to explain merotropic reactions,[3] and endeavors to show that they are in opposition to the experimental results which he has obtained in the investigation of the urazoles. The principal reasons given by Acree for assuming that the reactions proceed through the union of the anions of the urazole salts with the halide are as follows:

1. The free urazoles should give much lower velocity constants than their salts in solutions of the same concentration, since "organic acids are, as a rule, much less dissociated than their sodium salts."[4] This explanation is untenable, since it leads to the conclusion that the velocity of alkylation of organic acids should increase with their acidity constants, while,

[1] This Journal, **37**, 78.

[2] *Ibid.*, **37**, 83. Ber. d. chem. Ges., **41**, 3207.

[3] In a merotropic reaction a substance which exists only in one form passes over into a *derivative* of an isomeric form. See Michael: J. prakt. Chem., **42**, 19; **44**, 125. This Journal, **14**, 487. Ann. Chem. (Liebig), **363**, 20.

[4] Acree and Shadinger: This Journal, **39**, 234.

as is well known, the alkylation of organic acids cannot be realized under such conditions, quite irrespective of the value of such constants. The comparison between organic acids, on the one hand, and urazoles and their salts, on the other, is unwarranted. The free urazoles are amphoteric substances[1] and that they react with alkyl halides is due to their basic and not to their acidic nature. As bases they must show an affinity for halhydric acid, and the formation of the alkyl derivatives is due to this affinity.

2. If the reactions are ionic and independent of the nature of the cation, the metallic urazole salts should give "reaction constants, the values of which are directly proportional to the percentages of dissociation of the salts at the same concentration."[2] In confirmation of this statement, the following data are to be found in Acree's papers: The values of k_1 for the action of ethyl iodide (0.2 N at 25°) on the sodium, barium and magnesium derivatives of phenylthiourazole are 0.36, 0.32 and 0.42. Acree remarks that the velocity constants of the sodium and barium salts "agree very well with the amount of dissociation, but the constant for magnesium 1-phenyl-3-thiourazole is apparently high."[3] In 0.2 N solutions of sodium and barium nitrates (at 18°) the salts are dissociated 78.7 and 60.9 per cent., whereas the relation calculated from Acree's experiments is 78.7 and 71.1. With the sodium and magnesium salts, Acree's results would lead to dissociation values the exact reverse of those actually found. In a later paper,[4] the values of k_1 for the action of ethyl iodide on the sodium, potassium, barium and zinc salts of 4-methylphenylurazole (3 N in 40 per cent. alcohol at 60°) were found to be 0.42, 0.36, 0.28 and 0.05. If we take into consideration that the percentage dissociation of sodium and potassium nitrates in 0.2 N solution is practically the same (78.7), that of the barium salt is 60.9, and those of sodium, potassium and zinc chlorides (0.2 N) are 81.1, 83.6 and 69.1,

[1] Acree: This Journal, **38**, 346. Ber. d. chem. Ges., **41**, 3225.
[2] Acree and Shadinger: This Journal, **39**, 232.
[3] *Ibid.*, 234.
[4] Acree: Ber. d. chem. Ges., **41**, 3215.

it is obvious that the results[1] obtained by Acree in the alkylation experiments serve as better evidence against, than for, the assumption that such reactions are ionic in character.

3. If the reactions are ionic, the addition of an electrolyte to the urazole-alkyl halide solution should partially suppress the ionization of the urazole salts and therefore cause a decrease in the values of the velocity constants.[2] The nature of the influence that neutral salts exert on the velocity constants in certain reactions is still a matter of speculation.[3] Acree's argument is based on the original explanation given by Arrhenius, but this investigator, at least in the classical instance of the influence exerted by neutral salts on a mixture of acid and sucrose, has apparently abandoned the hypothesis and now assumes that the alteration in the reaction velocity is due to the added electrolyte increasing the osmotic pressure of the sugar.[4] As a means for determining the mechanism of organic reactions, this method has led to results so contradictory among themselves that its importance as a basis for theorizing cannot be regarded as in any sense satisfactory. Thus, Schwab[5] and Senter[6] have shown that neutral electrolytes, when added to a mixture of sodium chloracetate and sodium hydroxide, greatly increase the reaction velocity constants, and Steger[7] has further shown that sodium iodide exerts no influence on the reaction velocity between *o*-dinitrobenzene and sodium ethylate. Acree[8] himself

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[1] The above values are calculated on the assumption that complete ionization is practically reached at a dilution of 10,000 liters. Kohlrausch (Z. Elektrochem, **1907**, 342) has recently discussed this subject.

[2] Acree and Shadinger: THIS JOURNAL, **39**, 231.

[3] See Caldwell: P. Roy. Soc., **78**, 272. Geffcken: Z. physik. Chem., **49**, 257. Senter: J. Chem. Soc., **91**, 462.

[4] See Senter: *Ibid.*, **91**, 463.

[5] van't Hoff: Etudes, 26 and 113.

[6] J. Chem. Soc., **91**, 470.

[7] Z. physik. Chem., **49**, 333.

[8] Ber. d. chem. Ges., **41**, 3219. Acree attempts to explain this discrepancy by assuming that sodium iodide acts catalytically, but the salts in question are too nearly related chemically for this suggestion to be accepted as valid. The majority of the concordant results were obtained with the thiourazoles, but since organic thio derivatives have a marked tendency to unite with various substances, to form double compounds, it is evident that the first step in investigations of this nature is to ascertain whether the added electrolyte can unite with any of the components of the system to form such a product, since its formation must result in a change of energy, which in turn must necessarily affect the velocity constant.

shows, that potassium iodide decreases the value with sodium 4-methylphenylurazole, while sodium iodide increases it.

There thus appears to be no valid evidence in support of Acree's view that the reactions in question proceed through union of the anions of the salts with the alkyl halides. Acree[1] considers as Comstock's theory the view that when silver and potassium salts lead to isomeric alkyl derivatives these salts have structures corresponding to those of the alkyl derivatives. This view dates back, however, years before the appearance of Comstock's papers; indeed 22 years ago the writer,[2] in discussing this subject, assumed it was generally known, and showed that even at that time it was not tenable. Acree[3] believes that this view is improbable in the urazole reactions, but considers it a valid explanation in those reactions where only one of the possible isomers is formed. The proof put forward by the writer[4] in 1888, that the structure of a metallic salt does not necessarily follow from that of the alkyl derivative obtained from it, has already, for some years, met with general acceptance, and the older view, incorrectly denoted by Acree as "Comstock's theory," has been abandoned.

How incompatible the latter view is with the law of entropy is evident from the following example. Potassium benzamide gives N-, and the silver derivative O-alkylbenzamide; hence, according to the hypothesis in question, the first salt is a N- and the latter an O-derivative. Now, the adoption of these structures involves the assumption that the substance containing potassium is derived from the neutral, or practically neutral, keto form, notwithstanding that the potassium in such a structure would contain an enormous amount of free *chemical* energy and that its affinity for the oxygen is very much greater than for the nitrogen. On the other hand, the very weakly positive silver $(AgOH = 1 \times 10^{-4})$ is assumed to exist in the enolic, *i. e.*, acidic, form, although it

[1] THIS JOURNAL, **37**, 78. Ber. d. chem. Ges., **41**, 3204.

[2] J. prakt. Chem., N. F., **37**, 520. All that Comstock did was to apply this view (at one time very generally accepted) to explain his own experimental results.

[3] Ber. d. chem. Ges., **41**, 3205.

[4] J. prakt. Chem., N. F., **37**, 473.

may be made from the potassium derivative by double decomposition, and its affinity for oxygen is much less than that of potassium.

"Wheeler's theory" to explain tautomeric reactions is quoted by Acree[1] as follows: "When one salt yields with a certain reagent two products, one is formed directly and the second by rearrangement of the first." Wheeler,[2] in 1899, generalized an observation that Knorr[3] had previously made with more complicated derivatives, *viz.*, certain derivatives of the imidoester type, which are stable under conditions of temperature where addition of an alkyl iodide causes a rearrangement into the *N*-derivatives. Wheeler explained this change in two ways: the halogen of the halide united with the carbon, and the alkyl with the nitrogen of the —C = NH— group; or, the alkyl halide adds to the imido group to form an ammonium derivative; in either case the product thus formed breaks down into a *N*-alkyl derivative and alkyl halide. He concludes that "The tautomeric reaction in these cases, as in others, is undoubtedly nothing but a reaction by addition,"[4] but there is no indication in the papers of this investigator that this explanation was intended to serve as a general theory for tautomeric changes, as stated by Acree,[5] and it is so obviously impossible to use it for this purpose that the subject will not be discussed.

[1] This Journal, **37**, 78. Ber. d. chem. Ges., **41**, 3205.

[2] This Journal, **21**, 187; **23**, 135; **30**, 38.

[3] It appears to have escaped attention that a strict proof of the intermediate formation of an addition product in these rearrangements may be found in the earlier experiments of Knorr, who (Ber. d. chem. Ges., **30**, 929) showed that the O-*ethyl* derivative of α-quinoline is converted by methyl iodide, slowly in the cold, quickly and completely in the heat, into the N-*methyl* derivative. Later, Wheeler (This Journal, **23**, 139) showed that when isobutylimidobenzoic ester is heated with methyl iodide it yields benzmethylamide. The fundamental reason for this rearrangement is the increase of entropy brought about when the *O*-derivative, which has the smaller heat of formation, passes over into the *N*-isomer. If we change the structure of these substances so as to decrease the chemical resistance to the change, or to increase the affinity of the migrating radical for the atom to which it wanders, which in the case of the imido esters is done by introducing an alkyl into the imido group—the rearrangement may be brought about more readily, *i. e.*, by heat alone (Wislicenus and Goldschmidt: Ber. d. chem. Ges., **33**, 1467). Thermochemical work is in progress for placing this view (which is applicable to every case of intramolecular rearrangement) on a better experimental basis than the data at hand afford.

[4] This Journal, **21**, 187.

[5] Ber. d. chem. Ges., **41**, 3205.

"According to Nef's and Michael's addition theories, the salt has one structure,"[1] and is derived from the enolic form of the merotrope.[2] This theory assumes that, when such a salt yields two isomeric derivatives, one of them is formed by direct substitution of the metal and the other by the spontaneous decomposition of an intermediate addition product.

Acree[3] criticizes the "addition theory" as follows: "This theory demands that under the same conditions of solution all the different salts should give a mixture of esters in which the ratio of the *O*-ester to the *N*-ester is a constant," since the metallic ion should not affect the course of the reaction. Different urazole salts, however, "give widely different ratios of *O*-ester to *N*-ester, and hence Nef's and Michael's addition theories are inadequate."

This criticism is based on an inadequate knowledge of the "addition theory," and is not substantiated by Acree's ex-

[1] Acree: THIS JOURNAL, **37**, 81. In Acree's paper in the Ber. d. chem. Ges. (**41**, 3206) the statement is made that the addition theory was arrived at independently by Nef. This theory was published by the writer (J. prakt. Chem., N. F., **37**, 473) in 1888, and developed at that time so as to include practically all important tautomeric reactions known at that time. Three years later, Nef (Ann. Chem. (Liebig), **266**, 52) reproduced the writer's views; partially unchanged, partially in a slightly modified form. The changes which Nef made in this theory have never been accepted, and were untenable at the time of their publication (see THIS JOURNAL, **14**, 520). *Although Nef was thoroughly acquainted with the writer's paper, he failed to state that he was simply reproducing the ideas of another chemist, and, as his article was published in a widely read journal, it is sometimes believed that he really has some claim to the origination of the "addition theory."*

[2] This statement is quite as inaccurate as the above. The theory that merotropic keto derivatives, when converted into salts, become enol derivatives, was originated and widely developed by the writer in 1888, in the same paper as the "addition theory," and was only connected with it, inasmuch as the latter is necessary to explain the reactions of such enolic salts. During the succeeding four years (1892), *Nef persistently claimed that no structural change occurs in such reactions,* and then (Ann. Chem. (Liebig), **270**, 330) suddenly changed his opinion regarding the structure of the metallic derivatives of the nitroalkanes and accepted those which the writer (J. prakt. Chem., N. F., **37**, 507) had previously assigned to these salts. *Here, again, Nef used his method of silent appropriation. Although he now adopted the very principle, which only a year previously* (*Ibid.*, **266**, 56) *he had declared untenable, the reader is led to believe in this and in his subsequent papers* (see Claisen: *Ibid.*, **291**, 43, footnote) *that this idea originated with him.* While the writer consistently developed a general theory and showed its wide application and importance in organic reactions, the phenomenon remained a haphazard relation with Nef; thus acetacetic ester and hydrocyanic acid (see Michael and Hibbert: Ann. Chem. (Liebig), **364**, 70), as well as their sodium derivatives, are supposed to be enolic derivatives. The writer's views on this subject have been incorporated into accepted chemical theory, while those which may be said to belong to Nef have not been adopted.

[3] THIS JOURNAL, **37**, 82.

perimental results. The "addition theory" does not demand that under the same conditions of solution these metallic salts should give a constant ratio of O-to N-derivative, but is historically the first explanation why such a relation may depend on the metal in the salt; nor is it connected with the fact, as stated by Acree,[1] that in solutions these metallic salts contain the same anion. Furthermore, the results which Acree has obtained by using the same alkyl halide and those urazole salts which were under the same conditions in solution show a ratio between N- and O-alkyl derivative so closely together that, considering the rough method used in determining the ratios,[2] one cannot say with any certainty to what extent they differ. The silver salt alone gives a decidedly different ratio, but, as it is practically insoluble in the solvent employed, it cannot be considered as being "in the same condition of solution;" moreover, that silver salts often give different results is one of the oldest known facts in the field of tautomerism and one which the writer[3] explained by means of the "addition theory."

Addition was assumed to take place in two different ways: (*a*) When the substance contains, besides the metal, nitrogen or sulphur in a condition similar to that of these elements in ammonias or methyl sulphide, a substituted ammonium, or sulphonium, halide is primarily formed, which breaks down into a metallic halide and a merotropic alkyl nitrogen, or sulphur, derivative;[4] or, (*b*) in such compounds, where the addition of the reagent to a single unsaturated atom is constitutionally impossible, for instance with sodium acetacetic ester, $CH_3 — CONa = CH — COOC_2H_5$, addition takes place by breaking a double bond with subsequent breaking down of the addition product.[5] Acree,[6] in discussing the application of this theory to the alkylation of the urazoles, wrongly ascribes to it an addition of the parts of the halide "to the

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[1] Ber. d. chem. Ges., **41**, 3207.
[2] *Ibid.*, **41**, 3223.
[3] J. prakt. Chem., N. F., **37**, 520 (1888)
[4] *Ibid.*, **37**, 508.
[5] *Ibid.*, 487.
[6] Ber. d. chem. Ges., **41**, 3207.

double bond between nitrogens and carbons;"[1] an assumption which is theoretically improbable and not supported by the properties of such substances. Acree has also overlooked the fact that the writer has been engaged for many years in subjecting the "addition theory" to that final test of all speculation, *viz.*, to experimental verification, and has obtained results[2] which have led him to modify the "addition theory" in its original form very materially and to endeavor to connect it with the law of entropy.

In considering the merotropic relations of the urazoles from the point of view of the present "addition theory," it will be assumed that a considerable change in the energy and affinity relations of atoms in these substances does not occur in the formation of the ring,[3] an assumption which appears probable from their properties. The discussion of the relations will therefore be based on the chemical nature of the two characteristic radicals contained in the urazoles; *viz.*, that of a symmetrical diacylphenylhydrazide, on the one hand, and that of an imide of a very weak dibasic acid on the other. The acid imides give enolic sodium derivatives, but, even with an imide of a strong dibasic acid, such salts are easily hydrolyzed by water. The phenylhydrazides also readily give enolic sodium derivatives, which show, however, a greater stability towards water. Phenylurazole may exist in a keto and in 3 mono-enolic forms:[4]

[1] THIS JOURNAL, **37**, 81.

[2] J. prakt. Chem., N. F., **60**, 316–325; **68**, 492. Ber. d. chem. Ges., **33**, 3731; **34**, 4028; **38**, 23, 1922, 2083, 2096, 3217. Ann. Chem. (Liebig), **363**, 66.

[3] J. prakt. Chem., N. F., **79**, 418.

[4] Acree (THIS JOURNAL, **38**, 1) has examined the behavior of phenylurazole, and certain of its derivatives, towards diazomethane in ether solution, and concludes that phenylurazole exists in such solution mainly as D (see next page) although this form is in equilibrium with E and F (perhaps also with the dienolic form) present in relatively small proportions. The discoverer of diazomethane, von Pechmann (Ber. d. chem. Ges., **30**, 646), proved that it is not a trustworthy reagent to distinguish between keto and enol derivatives, a view which has since been confirmed (Michael and Hibbert: Ann. Chem. (Liebig), **364**, 70).

Diazomethane has an extremely large content of free *chemical* energy, which gives it a great reactivity and enables it to perform a very considerable chemical work at ordinary temperature. The question, whether it will react to give a merotropic methyl derivative of the substance depends on the affinity of its methylene group to those atoms in the merotropic substance that may unite with it. Its great capacity for performing chemical work makes it powerful, however, in effecting rearrangements, if the affinity relations do not permit the formation of the methyl derivative corre-

$$C_6H_5-N\overline{\qquad}NH$$

OC   CO

NH

C.

$$C_6H_5-N\overline{\qquad}N$$

OC   COH

NH

D.

$$C_6H_5-N\overline{\qquad}NH$$

OC   COH

N

E.

$$C_6H_5-N\overline{\qquad}NH$$

HOC   CO

N

F.
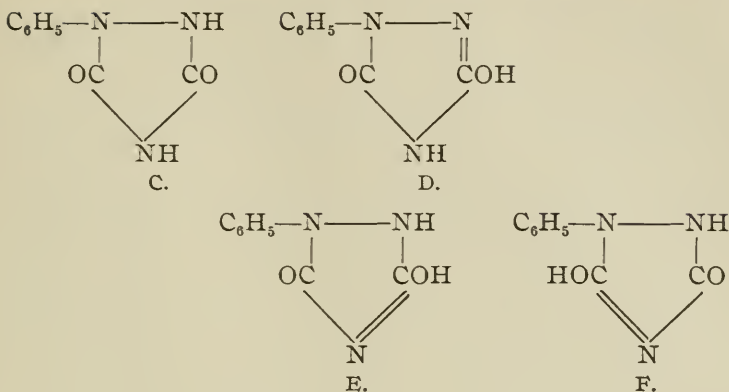
It is apparent that D, which is the enolic form of the hydra-
zide radical, should represent the most acidic of the enolic
structures; indeed, it has been proven experimentally by Acree
and Shadinger[1] that the acidity constants of urazole deriva-
tives of the type D are several hundred times greater than
those of E and F. Since the chemical resistance to enoliza-
tion by alkalies of imides and hydrazides is extremely
slight, the keto form (C), when treated with aqueous alkali,
in equivalent proportion, should contain the sodium deriva-

sponding to the structure of the tautomer under examination. Thus, von Pechmann
showed that diazomethane converts acetacetic ester, which is a stable keto deriva-
tive, into the enolic β-methoxycrotonic ester; obviously because the negative influ-
ence of the azo group in the reagent and of the acetyl and carbethoxyl groups in the
ester have greatly diminished the affinity of carbons in the two methylene groups.
When this negative influence is less pronounced in the substance, as, for instance, in
aldehyde, diazomethane is able to readily replace the hydrogen directly joined to car-
bon by methyl. Some chemists, H. Meyer (Monatsh., **25**, 1193), Peratoner and Pal-
azzo (Centralb., **1908**, I, 21), and Acree have been misled by the great reactivity of
diazomethane into believing that it can be successfully used as a tautomeric reagent,
whereas it is debarred through this very property (see Michael and Smith: Ann. Chem.
(Liebig), **363**, 39). Free phenylurazole, like free cyanic and cyanuric acids, is undoubt-
edly a keto derivative (C); the neutral, or almost neutral, character of these, and
analogous, products in this condition shows that the molecule in this form is intra-
molecularly better neutralized than when it is in the acidic form, and that the E ⟶ C
rearrangement proceeds with increase of entropy. Like cyanic acid (see Wolgast:
Diss., Leipzig, 1906), phenylurazole presents but slight chemical hindrance to enoliza-
tion; even water, though so slightly basic, is able through mass action to convert them
into acids which both have about the affinity constants of propionic acid. Cyanic
acid has been proven to have the keto form in ether solution (Michael and Hibbert:
Ann. Chem. (Liebig), **364**, 1291); in what forms the phenylurazole derivatives exist
in such a solution may perhaps be determined by their behavior towards amines (Michael
and Smith: *Ibid.*, **363**, 36).

[1] This Journal, **39**, 124.

tives of the 3 enolic forms, but, according to the "principle of partition,"[1] the quantitative amounts should stand in a relation to the acidity constants of these forms; that is, the solution should contain a large amount of the metallic derivative of the relatively strongly acidic D and very little of those of the weakly acidic E and F forms. Even this does not completely exhaust the theoretical possibilities with phenylurazole, since the NH group in the various forms may exhibit a slight acidity, in which case N-sodium derivatives should exist in the solution, although it is safe to say that the actual amounts of such derivatives would be inappreciable. With 4- and 2-methyl-1-phenylurazole the relations are comparatively simple; in aqueous solution the first substance and caustic soda in equivalent amount should give almost entirely the O-sodium salt corresponding to the D form, and the second a mixture of O-salts corresponding to the enolic forms E and F. These conclusions are very different from those reached by Acree,[2] who believes, for instance, that the metallic derivatives of 4-methylphenylurazole are mixtures of the N- and O-forms, and that the percentage of the O-form decreases with the positivity of the metal. Thus, with the strongly positive sodium, there is more N- than O-, and with the weakly positive silver, there is more O- than N-salt. Acree[3] has proven that the 4-methylphenylurazole has in aqueous solution almost the activity constant ($K = 1.1 \times 10^{-5}$) of propionic acid, and now assumes that this acid is converted, on the addition of caustic soda, to a considerable extent into a sodium salt derived from a much less acidic form! These results are incompatible with one another and also stand in contradiction to the law of entropy. The energy required to overcome the chemical resistance to the formation of any possible isomeric form of the metallic derivative is invariably subordinate to the increase of entropy, due to the more perfect neutralization of the large amount of positive

[1] Michael: J. prakt. Chem., N. F., **60**, 339. Ber. d. chem. Ges., **39**, 2138–2156, 2570, 2569; **40**, 140. When the "principle of partition" was first developed (J. prakt. Chem., N. F., **60**, 339) it was stated as a wide generalization of that involved in Thomson's "avidity principle."

[2] THIS JOURNAL, **37**, 83. Ber. d. chem. Ges., **41**, 3201, 3216.

[3] THIS JOURNAL, **39**, 126.

energy in the alkali or alkali metal by the most acidic form of the merotrope which can be formed.[1]

The fallacy in Acree's reasoning is obvious; it leads, for instance, to the impossible conclusion that in an aqueous solution of a very strong and an extremely weak acid, with insufficient alkali present for complete neutralization, we have much salt of the weak and only little of that of the strong acid. Equally fallacious is Acree's second conclusion, *viz.*, that the proportion of *O*-salt is greater with silver than with sodium; this would imply, to take a simple illustration, that a mixture of a very strong and a weak base, in solution with insufficient acetic acid for neutralization, would contain more acetate of the weak than of the strong base!

The merotropic relations of phenylurazole are evidently extremely complicated, and those of the 4- and 2-methyl derivatives which are much simpler and present the further advantage that Acree has studied their reactions quantitatively, will be discussed instead. Formanilide will be used as the standard of comparison for the hydrazide group, as the merotropic reactions of phenylhydrazides have not been sufficiently examined for our purpose.

The formation of ammonium salts depends on nitrogen having an affinity for hydrogen sufficient to give a certain stability to the ammonium radical, thus enabling the hydrogens to neutralize through the nitrogen and through space the negative energy of the halogen.[2] Since this process of neutralization takes place largely spatially, there must be bound *chemical* force in an ammonium halide between the hydrogens, as well as between the nitrogen and the halogen.[3] If we in-

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[1] This important law has been proven experimentally. Michael: Ber. d. chem. Ges., **33**, 3731; **38**, 22, 1922.

[2] Michael: Ber.d. chem. Ges., **39**, 2792, footnote. This Journal, **41**, 126.

[3] It is customary to assume, in the addition of hydrochloric acid or methyl iodide to ammonia, that there is a complete separation of the parts of the addenda; an assumption which is unproven and theoretically very improbable. Since bound *chemical* force exists between the hydrogen or methyl and the halogen in the addition products, the bound *chemical* force between the hydrogen or methyl and the halogen decreases during the process of addition only to the extent that it exists in the addition product, *i. e.*, an actual separation of the addenda into two parts does not take place. This conception of addition applies to all cases where bound *chemical* force exists between the parts of the addenda after the addition has taken place. That rearrangements like iso into tertiary butyl bromide do not, as will be experimentally shown in a later paper, proceed by dissociation and subsequent addition, but through the undissociated molecule agrees with this view.

troduce a formyl radical in place of a hydrogen in phenyl-ammonium iodide, we not only reduce the affinity of the remaining hydrogens, and the nitrogen, for the halogen, but also the neutralizing power of the ammonium radical; for this reason such salts show an extremely slight stability and the free amides are unable to overcome the considerable chemical resistance which accompanies the addition of an alkyl halide to an ammonia derivative.

What is the mechanism of the action of sodium on formanilide, and how does the introduction of the metal change the energy and affinity relations of those elements that may unite directly with the alkyl group, *i. e.*, of nitrogen and oxygen?

The sodium has afforded to it two points of attack: one on the nitrogen and one on the oxygen of the anilide, and, in either case, it has to overcome the resistance involved in the separation of hydrogen from the nitrogen.[1] The two factors that determine the chemical action, *i. e.*, the affinity of nitrogen and oxygen for sodium and the free *chemical* energy in these atoms, exist evidently much more developed in the oxygen than in the nitrogen of the anilide and these relations permit the direct formation of *O*-sodium formanilide, which represents the maximum entropy of the system:

$$2C_6H_5.NH.\overset{\overset{\textstyle H}{\textstyle |}}{C} : O + Na_2 = 2C_6H_5.N : \overset{\overset{\textstyle H}{\textstyle |}}{C}.ONa + H_2.$$
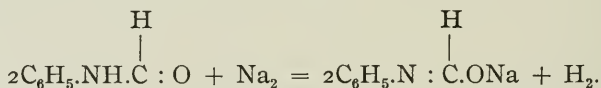
The energy and affinity changes that occur with the introduction of sodium into formanilide are as follows: as a derivative of a very weak acidic substance, *i. e.*, of enol formanilide, the positive chemical energy of sodium is only imperfectly neutralized, and, as the metal enters into direct chemical union with the oxygen, that element must lose much of its free *chemical* energy in the process. On the other hand, the bound *chemical* force, which in the anilide held the nitrogen and the subsequently liberated hydrogen in chemical union, has been partially transformed in the salt into free *chemical*

[1] Michael: Ber. d. chem. Ges., **34**, 3731; **38**, 1933.

energy in the nitrogen. Further, not only has the introduction of sodium increased the free *chemical* energy of the nitrogen, and decreased that of the oxygen, but it has converted the negative —CHO (formyl) into the strongly positive CHONa group and, thereby, greatly increased the affinity of the nitrogen for alkyl. For these reasons the "polymolecule," which is first formed in the action of methyl iodide on sodium formanilide, decomposes with formation of the *N*-derivative; and as this has a greater heat of formation than the isomeric *O*-product, the maximum entropy of the system is thus directly realized:[1]

$$
\begin{array}{ccc}
C_6H_5.N \longleftarrow CH_3 & & C_6H_5.N.CH_3 \\
\parallel \qquad\quad | & = & | \qquad\quad + NaI. \\
HCONa \longrightarrow I & & HCO
\end{array}
$$
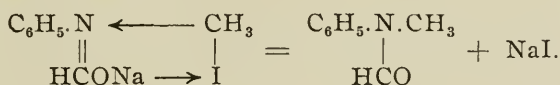
By introducing into sodium formanilide the weakly positive silver (AgOH $= 1 \times 10^{-4}$), in place of the very strongly positive sodium, a relative change in the affinity relations of the nitrogen and oxygen for methyl in favor of the latter element takes place. The silver is much less able than the sodium to neutralize the effect caused by the introduction of formyl into aniline and the free *chemical* energy in the oxygen. The formation of a *N*-derivative is prevented by the alteration in the affinity values; owing to the second and the strong affinity between silver and iodine, the reaction proceeds with the formation of the *O*-derivative:

$$
\begin{array}{cc}
C_6H_5.N : CH.O \longleftarrow CH_3 & \\
| \qquad\qquad\quad | & = C_6H_5N : CHOCH_3 + AgI. \\
Ag \longrightarrow I &
\end{array}
$$
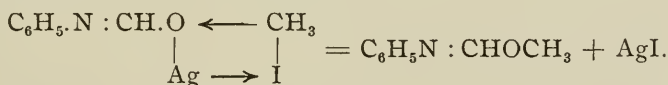
With methyl iodide and sodium 4-methylphenylurazole, 96–97 per cent., and with ethyl iodide, 92–94 per cent., of *N*-alkyl derivative is formed.[2] These results are not only

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[1] There appears to be no valid reason for assuming the intermediate formation of a substituted alkylammonium iodide in this reaction. It is more probable that the sodium, which is the most powerful positive force in the salt, acts directly in effecting the endothermic separation of the iodine from the methyl. The reason why methyl iodide reacts with such difficulty on neutral sodium salts of organic acids is that the free *chemical* energy in the metal and in the two oxygens of the carboxyl group has been largely converted into bound *chemical* energy and heat in the formation of the salt.

[2] Acree: Ber. d. chem. Ges., **41**, 3227.

in conformity with the "addition theory," but are also in close agreement with a principle developed some years ago,[1] *viz.*, that when alkyl halides react with salts to form mixtures of isomeric alkyl derivatives, the more positive the alkyl radical is, *i. e.*, the greater its tendency towards a metallic character, the greater proportion of that isomer will be formed whose structure is analogous to that of the metallic salt.[2] As far as is known, methyl and ethyl iodides react with silver formanilide to form exclusively *O*-alkyl derivatives; with silver 4-methylphenylurazole the first reagent gives a mixture of *N*- and *O*-derivatives in about equal proportions, while with the latter about 38 per cent. of *N*- and 62 per cent. of *O*-product[3] is obtained. The imido group in formanilide shows no capacity to add alkyl halides, while that in the hydrazide radical of the urazole does, and this tendency should increase somewhat with the introduction of the silver radical. These merotropic relations in the case of the silver urazoles are very similar to those of silver nitrite; in each case the silver salt of a weak acid, containing an unsaturated nitrogen, is extremely sensitive to a change in the alkyl radical and, here too, in agreement with the theory, the proportion of *O*-derivative increases with the relative positivity of the alkyl group.[4]

Similar results have been obtained by Acree[5] in the alkylation of the salts of 2-methylphenylurazole, where the acid imide group is involved in the reactions. The results obtained from the sodium salt and methyl and ethyl iodides are practically the same as those from the 4-methyl derivative; with the silver salt the first halide gives 87–90 per cent. and the second 48–50 per cent. of *O*-derivative. If, as is probable, the additive power of the imido group for alkyl halide in the acid imide group is less than that in the hydrazide radical, the proportion of *O*- to *N*-alkyl derivative should be greater

[1] Michael: J. prakt. Chem., N. F., **60**, 323.

[2] This is due to a change in the affinity relation favoring oxygen with increasing metallic character of the radical and to the fact that the difference between the heats of formation of the isomeric derivatives becomes less.

[3] Acree: Ber. d. chem. Ges., **41**, 3229.

[4] Von Meyer: Ann. Chem. (Liebig), **175**, 88. Tschenriak: *Ibid.*, **182**, 158.

[5] Ber. d. chem. Ges., **41**, 3232.

with the 2- than with 4-methylphenylurazole. This is indeed the case with ethyl iodide, but with methyl iodide it is almost the same with both urazoles, and this is the only one of Acree's results that awaits a satisfactory explanation.[1]

We pass now to a discussion of Acree's own hypothesis as an explanation of merotropic reactions. The small velocity constant of certain merotropes, in comparison to the large value of their metallic derivatives, is explained as follows: ''The weakly acid tautomeric amides, acetacetic ester, etc., react, as a rule, very slowly with alkyl halides, acid chlorides, etc., at ordinary temperature, because these weak acids furnish few *anions* of the tautomeric forms to react with the alkyl halides. The addition of bases, such as pyridine, alkalies or other metallic hydroxides, or sodium ethylate, causes an increase in the reaction velocity because the base forms, to a greater or less extent, depending on the strength of the acid or base, tautomeric salts of the amide, acetacetic ester, etc. These salts, because they are more highly ionized than the acid, furnish the solution with a greater concentration of the anions of the 2 or more tautomeric forms and hence the reaction velocity is increased.''[2]

Acetacetic ester is ionized to a slight extent in solution $(K = 2 \times 10^{-11})$,[3] as well as the acid amides, although the latter undoubtedly to a far less degree. They do not, as stated by Acree, react with alkyl halides at ordinary temperature, or at any temperature, in the sense implied in the above statement of Acree's. There is, furthermore, no relation between the extent to which enolic substances yield anions in solution and their capability of yielding alkyl derivatives, since the weakest and the strongest enols are inert in this respect. Nor is the behavior of these substances towards the acyl chlorides in agreement with Acree's views; acetacetic ester is very slightly ionized in aqueous solution and does not react at all to form an acetyl derivative, while the

[1] The acid imido group in the urazoles should show more capacity for adding alkyl halide than that in the imide of an ordinary dibasic organic acid, since it has the basic phenylhydrazine, whereas the latter has a neutral hydrocarbon, as the mother substance.

[2] Science, **30**, 21. Ber. d. chem. Ges., **41**, 3199.

[3] Goldschmidt and Scholz: Ber. d. chem. Ges., **40**, 624.

amines, which are undoubtedly still less ionized, react very readily.

To explain the formation of two isomers in the alkylation of certain metallic derivatives, Acree[1] assumes that they consist of a mixture of two tautomeric salts, and when the equilibrium of these salts is disturbed by chemical reaction—certain reagents showing a selective preference for one or the other form—it is immediately reestablished. Thus, sodium acetacetic ester is represented by the formula

$$CH_3.CONa : CH.COOC_2H_5 \rightleftharpoons CH_3.CO.CHNa.COOC_2H_5,[2]$$
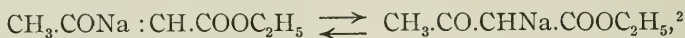
and gives an *O*- or *C*-derivative according to the selective taste of the reagent employed. This view represents a long step backwards, even when compared with the original conception as to the nature of the structural changes that take place in the conversion of acetacetic ester into its sodium derivative. Geuther supposed the formulas

$$CH_3.COH : CH.COOC_2H_5 \text{ and } CH_3.CONa : CH.COOC_2H_5$$
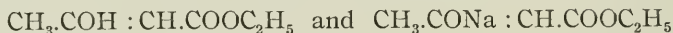
to represent the structures of acetacetic ester and its sodium derivative, while, up to 1888, the generally accepted Frankland-Wislicenus view assumed the forms

$$CH_3.CO.CH_2.COOC_2H_5 \text{ and } CH_3.CO.CHNa.COOC_2H_5.$$
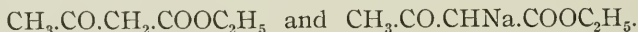
The writer[3] then showed that the chemical relations of these substances could be explained only by accepting the formula

$$CH_3.CO.CH_2.COOC_2H_5,$$

for the ester, and

$$CH_3.CONa : CH.COOC_2H_5$$
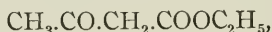
for the salt. After explaining why a compound having a structure represented by

$$CH_3.CO.CHNa.COOC_2H_5$$

cannot be stable, but must undergo a spontaneous rearrangement, the metal passing over to oxygen, the following statement was made: "Es lässt sich aber nicht verkennen, dass

[1] This Journal, **37**, 78. Ber. d. chem. Ges., **41**, 3210.
[2] This Journal, **37**, 77.
[3] J. prakt. Chem., N. F., **37**, 473. This Journal, **10**, 158; **14**, 481.

eigentlich zwei isomere, stabile Natriumacetessigäther aus der unbeständigen Verbindung entstehen sollten, da der stark negative Carbonylsauerstoff des Carbäthoxyls gewiss eine bedeutende Verwandschaf tauf das Natrium ausübt. Demnach sollte neben der Verbindung

$$CH_3.CONa : CH.COOC_2H_5$$
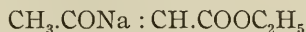
auch eine gewisse Menge von

$$CH_3.CO.CH : C(ONa)OC_2H_5$$
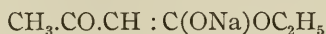
entstehen.''[1] That an alcoholic solution of sodium acetacetic ester must contain some of the latter sodium derivative will be obvious on considering that malonic ester is readily converted by sodium ethylate into the enolic sodium derivative, and that acetacetic ester may be looked upon as derived from malonic ester by replacing one of the carbethoxyl groups by the more acidic acetyl group. It follows, therefore, from the principle of partition, that an alcoholic solution of sodium acetacetic ester is a mixture of the above enolic derivatives, in which the $CH_3.CONa : CH.COOC_2H_5$ form greatly preponderates, since the enol form from which it is derived is much more acidic than the enol form of the malonic ester type. A chemical system can change spontaneously only when it is accompanied by an increase of entropy, and it is extremely improbable that the equation

$$CH_3.CO.CH_2.COOC_2H_5 + C_2H_5ONa =$$
$$CH_3.CO—CHNa.COOC_2H_5 + C_2H_5OH$$
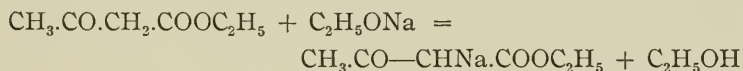
represents such a change. Even if we assume the formation of such a *C*-sodium derivative, its concentration would be exceedingly small and only if the two enolic sodium acetacetic esters were inert toward the reagent would we be justified in assuming that the reaction proceeds through the salt with the smallest concentration. Owing to the very slight acidity of the enol acetacetic esters, the content of free *chemical* energy in their sodium derivatives must be very great and it is safe to say that, even with a reagent so comparatively inert

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[1] J. prakt. Chem., N. F., **37**, 488.

as alkyl iodide,[1] the reaction would proceed practically through the enolic salts, notwithstanding the presence of a trace of the keto salt and the fact that the latter would have a still larger content of energy.

However, a theory that proposes to explain the behavior of the metallic derivatives of merotropes should at least be able to connect the chemical character of the substances with those of the reagents, as well as be in harmony with the course of the reactions. The application of Acree's views to the acet-acetic ester reactions leads to inconsistent conclusions. For example, ethyl iodide, chlorcarbonic ester and acetyl chloride react with sodium acetacetic ester, with formation of a C-, a mixture containing much O- and little C-, and a C-derivative, the reactivity of the reagents following the order stated above.[2] In explaining the urazole reactions, Acree assumes that the ratio of the tautomeric alkyl derivatives formed in the reaction stands in a relation to the proportion of the tautomeric salts originally present. From this point of view, the behavior of ethyl iodide and acetyl chloride proves that sodium acetacetic ester is a C-derivative, while, accord-ing to the action of chlorcarbonic ester, it is present largely in the O-form. To state, as Acree does, that certain reagents exert a "selective affinity" for one or the other tautomeric form, partakes more of tautology than of a scientific explanation, but this view also leads to conclusions that are contradictory among themselves. Thus, according to Acree's view, ethyl iodide "selects" the C-sodium acetacetic ester, while chlor-carbonic ester (a much more reactive reagent) favors the O-derivative, notwithstanding that the latter contains less positive energy than the C-salt; finally, acetyl chloride, which is still more reactive, "selects" the C-salt.[3]

Besides the objections mentioned above, Acree believes that his experimental results, while they support his own views, disprove the "addition theory" in a number of other respects. From the latter hypothesis it would have been

[1] See Michael: Ber. d. chem. Ges., **38**, 3223.

[2] Ber. d. chem. Ges., **41**, 3216.

[3] For explanations of these reactions, based on the law of entropy, see Michael: Ber. d. chem. Ges., **38**, 1922, 2083, 2097, 3217. J. prakt Chem., N. F., **72**, 542.

possible to predict the possibility of a change in the ratio of N- to O-alkylphenylurazole by changing the nature of the solvent. Thus, with silver 4-methylphenylurazole and ethyl iodide in ether, alcohol, acetone and water, 35, 33, 39 and 37 per cent. of the N-derivative are formed.[1] Acree states that these slight differences may be due to changes caused by the solvent in the relative reactivities which the two anions show towards the halide, or that the value of K_3 changes with the solvent, a view which appears more a restatement of the facts in other terms than a satisfactory explanation. When we consider that Menschutkin[2] has shown that the additive power of triethylamine for alkyl halide depends on the solvent present, and that the ratio of N-derivatives formed in the urazole reaction depends on the additive power of the nitrogen in question, it is apparent that, with a substance so sensitive to changes as the silver urazole derivative, it would have been possible to predict Acree's results from the "addition theory."

The constancy of the ratio of N- to O-alkylurazoles in the action of ethyl iodide on potassium and silver 4-methylphenylurazole between 22° and 90° is an objection to the "addition theory."[3] It is in agreement with Acree's views and for the following reasons: "Der negative Temperaturkoeffizient für die Dissoziation der beiden tautomeren Salze ist, wie bereits Jones und West, wie auch Noyes und Coolridge, nachgewiesen haben, nur sehr klein und ausserdem bei allen Salzen nahezu der gleiche."[4] Acree's results show, however, that the proportion of N-derivative, instead of being constant, varies up to 5 per cent., that is, the effect of change in temperature is greater than that caused by change in solvent, which Acree, on the same page in his paper, had emphasized as important. Furthermore, the change in the dissociation of tautomeric salts with temperature has never been investigated[5] and there is no evidence at hand which enables us to say whether the tem-

[1] Acree: Ber. d. chem. Ges., **41**, 3216.
[2] Z. physik. Chem., **6**, 41.
[3] Acree: THIS JOURNAL, **37**, 82.
[4] Ber. d. chem. Ges., **41**, 3216.
[5] The statement quoted above from Acree's paper leads one to believe that tautomeric derivatives have been examined by Jones and West and Noyes and Coolridge, but this is not the case.

perature coefficients of conductivity of two products so different in their chemical character as the sodium *O*- and *N*-urazoles must be is so small as Acree assumes. Why it should follow from the "addition theory" that the above changes in temperature should cause a greater variation in the *N*- and *O*-ratios than Acree found, the writer is unable to understand and he cannot consider these results an objection to that theory.

According to Acree,[1] a change in the concentration of the substances in these urazole reactions does not cause an appreciable variation in the ratio of *N*- to *O*-derivative; thus, with sodium 4-methylphenylurazole and ethyl iodide, or allyl iodide, although the concentration was decreased four times the ratio remained constant at 94 : 6 and 98 : 2. This result also agrees with his views, since the *N*- and *O*-sodium salts have similar dissociation values. Only with allyl iodide are experimental data quoted in Acree's paper;[2] in one experiment with 10 parts dilute alcohol 97.7 per cent., and in 4 others with 20 parts of solvent 96.7 to 99.1 per cent. *N*-derivative were formed. Acree[3] has described his method for determining the above ratio, according to which the product of alkylation is subjected to a long series of operations, the insoluble residue finally obtained being the *O*-derivative. As the total product in the above experiments was about 0.2 gram, and the final insoluble product about 0.004 gram, it is difficult to understand how Acree could venture to draw the conclusion stated above from such slight experimental material. Acree's statement,[4] moreover, that the *N*- and *O*-sodium urazoles should have similar dissociation values does not agree with the chemical character of derivatives analogous to such substances. The first salt, being derived from the keto form, should be largely hydrolyzed in dilute alcoholic solution, while the second, which is derived from an acid having about the acidity constant of propionic acid, should be only slightly hydrolyzed. It is also obvious that such experi-

[1] Ber. d. chem. Ges., **41,** 3218.
[2] *Ibid.*, 3228.
[3] *Ibid.*, 3223.
[4] *Ibid.*, 3218.

mental results do not in any way disprove the "addition theory," as claimed by Acree, nor does it follow from this theory that a change in concentration should cause an appreciable variation in the N- to O-ratio.[1]

In support of his views, Acree quotes a number of investigations by other chemists, but the confirmation is more apparent than real, since some of the results are inaccurately stated, and the others are inapplicable to illustrate "the use of selective reagents in proving the presence of two tautomeric salts."[2]   Hantzsch's work on phenylnitromethane, and Wislicenus' on formylphenylacetic ester are selected.   According to Acree,[3] Hantzsch showed that the first substance dissolves in alkali, forming, besides $C_6H_5CH : NO(ONa)$, a small proportion of $C_6H_5CHNaNO_2$.   In reality Hantzsch did not prove the presence of a C-derivative but emphasizes that the solution contains only O-salt.[4]   Acree also states that if the salts of the tautomeric phenylnitromethanes "exist in tautomeric forms in solution," then "we should be able to select an acid weak enough to precipitate the more weakly acid tautomeric form," but not the stronger acid form,   while "a strong mineral acid would precipitate both tautomers."[5] Hantzsch's experiments "amply verify this point.   Carbonic acid precipitates the true phenylnitromethane from solutions of its alkali salts, whereas strong acids precipitate the more strongly acid isonitro form, nearly pure."[6]   There is nothing in Hantzsch's researches, or in his theoretical views, to justify such statements.   Hantzsch[7] states that the keto form is a

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[1] Acree (Ber. d. chem. Ges., **41**, 3217; This Journal, **37**, 85) also claims that his views enable one to "predict" that different alkyl halides should show varying reaction coefficients and that the proportion of N- to O-derivative may depend on the nature of the halide. These are subjects which have often been discussed previously (see J. prakt. Chem., N. F., **37**, 521; **60**, 319, 368) and the writer fails to see that Acree has in any way contributed to a better understanding of them, or why it should be necessary to "predict" a relation that previous investigators have already put on an experimental basis.

[2] This Journal, **37**, 76.

[3] *Ibid.*, **38**, 33.

[4] Ber. d. chem. Ges., **32**, 2257.

[5] This Journal, **37**, 76.

[6] *Ibid.*, 77.

[7] Ber. d. chem. Ges., **29**, 2257.

neutral substance, and explains the behavior of the alkali
salt towards carbonic acid and strong acids in a manner which
is not open to doubt, *viz.*, carbonic acid, in comparison to the
isonitro derivative, is so weak an acid that only traces of
the first body are liberated, which isomerize to the neutral form;
as the equilibrium between carbonic acid and the iso acid
is thereby disturbed, the reaction proceeds with further separa-
tion of traces of the isonitro body and simultaneous isomeriza-
tion.   On the other hand, strong acids · precipitate the iso-
nitro acid practically completely, and so nearly instantaneously
that it has not time to isomerize.

Equally inaccurate and misleading are Acree's statements
with regard to formylphenylacetic ester. W. Wislicenus[1]
originally regarded the two modifications of this substance,
also those of certain of their metallic derivatives, as tauto-
meric; Hantzsch[2] accepted tautomerism for the ester and
suggested stereoisomerism for the salts, while Knorr[3] as-
sumed the esters as well as the salts to be isomers.
Wislicenus[4] subsequently gave up his first view in favor of
that of Hantzsch. The writer[5] showed later that the solid
modification (72°) of Wislicenus is a mixture of two desmo-
tropes (50° and 100°) and that the three desmotropes are all
enolic. The liquid form was shown to be stable towards
carbonic acid but not towards dilute sulphuric acid, while the
modification melting at 50° is stable towards dilute and that
at 100° stable towards strong sulphuric acid, which behavior
explains why the desmotropic form precipitated from the salts
depends on the acid and its concentration. The above results
obviously give no support to Acree's views, or to his statement
that the salts are tautomeric and are present as such in equi-
librium in the solution.

Acree[6] indeed believes that with "proper solvents and ex-
perimental conditions both forms" of the tautomeric salts

[1] Ann. Chem. (Liebig), **291,** 147.
[2] Ber. d. chem. Ges., **29,** 2266.
[3] Ann. Chem. (Liebig), **306,** 377, footnote.
[4] *Ibid.,* **312,** 34.
[5] Ber. d. chem. Ges., **39,** 203.
[6] THIS JOURNAL, **37,** 84.

that exist in solution could probably be isolated, and, in support of this opinion, quotes, besides the research of Wislicenus mentioned above, that of Hantzsch and also of Titherly. Hantzsch[1] found that cyanuric acid, which is a keto derivative, dissolves in soda to form the merotropic O-salt. If this solution is kept at $0°$, and a soluble mercuric salt added, an O-mercury salt is precipitated, while at $100°$ we have a N-mercury salt formed, and between these temperatures a mixture of the isomeric salts results. The affinity relations of sodium and of mercury towards oxygen and towards nitrogen are exactly reversed; that is, with sodium there is a decrease from oxygen to nitrogen, while with mercury there is an increase. That the O-sodium salt at $0°$ gives an O-mercury, and at $100°$ a N-salt, shows that at the higher temperature the O-derivative is able to rearrange itself to the modification representing the maximum condition of entropy, and this fact offers no support to Acree's view, according to which the sodium salt in solution is a mixture of both forms.

Titherly[2] found that when caustic soda is added to an aqueous solution of silver nitrate and benzamide a white, stable silver derivative is precipitated, but if silver nitrate is added to sodium benzamide, both substances in alcoholic solution, an orange precipitate is formed, which quickly decomposes. Similar results were obtained with acetamide; the orange salt in the latter case is slightly more stable, however, and it was possible to make a silver determination, which gave a result agreeing approximately with that required for silver acetamide. These observations show that stable, white silver derivatives of known composition and structure, and very unstable, yellow products of unknown composition, structure and purity have been obtained, but they do not confirm Acree's views in any way. Acree[3] finds confirmation of his theoretical views, also, in the organic researches of Hantzsch and Caldwell and Scholl and Steinkopf, as well as in the physical-chemical researches of Burke and Donnan, Slator, Senter,

[1] Ber. d. chem. Ges., **35,** 2722.
[2] J. Chem. Soc., **71,** 486; **79,** 408.
[3] Ber. d. chem. Ges., **41,** 3210.

Euler and Hecht, Conrad and Brückner. These investigations are supposed to furnish experimental proof that organic reactions may be ionic in character, and as they are exerting an influence on organic theory, the writer deems it of importance to discuss them from the point of view of an organic chemist.

Hantzsch and Caldwell[1] treated silver nitroform with methyl iodide at $-75°$ and obtained an addition product of the formula $C(NO_2)_3Ag.2CH_3I$. This substance is decomposed by water, and by nearly absolute alcohol, at $-10°$, into nitroform; and when suspended in indifferent solvents it decomposes into trinitroethane (C-derivative) and silver iodide. Silver nitroform, which exists only in a hydrated condition, dissolves readily in ether and the solution gives, with methyl iodide, the C-derivative, with a trace of nitroform. Hantzsch and Caldwell explain these results by assuming that silver nitroform in ether solution reacts only in the ionic condition; to the nitroform ion $(C(NO_2)_3)$ methyl may add in two directions *i. e.*, either to oxgyen or to carbon, and the C-derivative is formed because it is the more stable of the two products. The addition product $(C(NO_2)_3Ag.2CH_3I)$[2] can only decompose intramolecularly, *i. e.*, as an undissociated complex, and, since the silver is joined to oxygen, the O-methyl derivative $(C(NO_2)_2=NO(OCH_3))$ is formed. The latter body is decomposed by water into nitroform and methyl alcohol, but in its absence it isomerizes to the C-derivative. These explanations are open to very serious objections. If the formation of the C-derivative depends on the existence of the nitroform anion, then potassium nitroform, which must be more dissociated in solution, should also give the same substance, but Hantzsch and Rinckenberger[3] showed that no reaction takes place. Further, if we accept the view that it is the nitroform anion which reacts in the formation of the methyl derivative, the further assumption that methyl may

[1] Ber. d. chem. Ges., **39**, 2473.

[2] The formation of this substance at a low temperature and its behavior at a somewhat higher temperature is an exceedingly interesting, experimental confirmation of the view, that in every reaction the primary step is the formation of a "polymolecule."

[3] Ber. d. chem. Ges., **32**, 628.

add *a priori* either to oxygen or to carbon is extremely improbable. The effect of 3 such negative radicals as NO_2, and which are joined directly to carbon, would be to greatly reduce the affinity of this carbon for methyl.[1] Thus, silver oxalacetic ester ($C_2H_5OOC.COAg : CH.COOC_2H_5$) and ethyl iodide give solely an *O*-ethyl derivative;[2] that is, even the radicals $COOC_2H_5$ and $CH.COOC_2H_5$ reduce the affinity of the Δ^β—C (C of the CH group) to such an extent that the reaction proceeds not by addition but by the direct substitution of silver. These organic radicals, however, exert, in comparison to NO_2, a very weakly negative influence, and it is therefore safe to say that the assumption that the nitroform anion[3] can unite with methyl to form a *C*-derivative is untenable. For the same reason, *viz.*, the reduction of the affinity of the unsaturated carbon for methyl due to the strongly negative radicals, a spontaneous isomerization,

$$C(NO_2)_2NO(OCH_3) \longrightarrow CH_3.C(NO_2)_3,$$
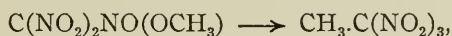
cannot be considered at all likely; nor is it probable that *O*-methylnitroform would be decomposed by almost absolute methyl alcohol at —100° in a short time into nitroform and methyl alcohol.[4] In view of these serious objections, Hantzsch's assumption that the alkylation proceeds through the anion of the salt cannot be considered at all probable. Hantzsch accepts the keto structure of nitroform as representing a neutral substance, but, if we lay stress on the great negative influence which must be exerted by 3 nitro groups on the methane hydrogen, it seems more probable that it represents an acidic substance. When we consider, further, the weakly basic properties of silver hydroxide ($AgOH = 1 \times 10^{-4}$) and that silver shows a decided affinity for carbon when the latter element is in a relatively negative condition,[5] it seems by no means unlikely that the intramolecular, atomic neutralization in $Ag.C(NO_2)_3$ is better than that in $C(NO_2)_2$:

[1] See J. prakt. Chem., N. F., **60**, 291, VIII. Ber. d. chem. Ges., **39**, 2142.

[2] Nef: Ann. d. Chem., **276**, 227.

[3] Hantzsch and Caldwell assume $C(NO_2)_3$ as the nitroform anion, but if silver nitroform has the O-structure the anion should be represented by $C(NO_2)_2N(O)O^-$.

[4] The analogous alkyl nitrates are quite stable towards alcohol.

[5] For instance in acetylene derivatives.

N(OAg). In this case the rearrangement of the *O-* into the *C*-derivative would represent an increase of entropy, and the stable silver derivative which is known contains the metal joined to carbon.[1] With such a derivative the action of methyl iodide alone, or in presence of a solvent that cannot furnish hydrogen for forming hydriodic acid, must lead to the formation of *C*-methylnitroform. Silver nitroform, like other silver salts, has a strong affinity for hydriodic acid, and, in the presence of solvents that can furnish hydrogen, for instance water or alcohol, the reaction may proceed more easily by the elimination of that acid from the halide and water, or alcohol, in which case nitroform would be set free, than through the direct substitution of silver.[2]

Scholl and Steinkopf[3] examined the reaction between silver nitrate and iodomethylcyanide. These substances unite to form a fairly stable addition product ($NCCH_2I,AgONO_2$), which is decomposed by boiling water into its components, and on dry distillation into silver iodide and the compound $NC.CH_2.ONO_2$. Here we have another interesting experimental verification of the theory that reactions proceed through the "polymolecule" phase.[4] That in the dry distillation of such a product the halogen unites with silver and is replaced by the nitrate group and that this double compound is decomposed by water into its components is certainly no evidence in favor of the reaction being ionic.[5]

Burke and Donnan[6] have studied the action of alcoholic silver nitrate on alkyl iodides. These reactions, as Nef[7] had previously shown, are very complicated; the metal in the nitrate may be replaced by alkyl, or, owing to the affinity of silver nitrate for hydriodic acid, alkenes may be formed,

[1] Ley and Kissel (Ber. d. chem. Ges., **32**, 1366) proved that mercuric nitroform in a solid state, or dissolved in indifferent solvents, is a *C*-derivative; in alcohol and water it is at least partially the *O*-salt.

[2] Nef (Ann. Chem. (Liebig), **309**, 140) showed that silver nitrate and alkyl halides in absolute alcoholic solution react to give, besides esters, free nitric acid to a very considerable extent. If *C*-silver, like *C*-mercury nitroform, is converted by water, or alcohol, into the *O*-salt, it would be structurally analogous to silver nitrate.

[3] Ber. d. chem. Ges., **39**, 4393.

[4] *Ibid.*, **34**, 4028; **39**, 2140. THIS JOURNAL, **39**, 3; **41**, 120.

[5] Acree: Ber. d. chem. Ges., **41**, 3214.

[6] J. Chem. Soc., **85**, 555.

[7] Ann. Chem. (Liebig), **309**, 140.

which, in presence of the nitric acid set free, may unite with the alcohols to form mixed ethers. The velocity constant is, therefore, dependent on the following relations; firstly, the relative ease of replacement of the iodine in the alkyl iodides by the nitrate group; secondly, the relative ease of elimination of hydriodic acid from the alkyl iodides by alcoholic silver nitrate. A further factor enters into the relative proportions of the reaction products, *viz.*, the relative facility with which the nascent, unsaturated alkenes may unite with the alcohol used as a solvent. The reaction between alcoholic silver nitrate and alkyl iodide forms, therefore, a complex subject for an investigation of the relations between the structure of the alkyl group and the process of substitution on the one hand, and that of elimination, complicated by that of addition, on the other. It is obvious that the determination of velocity constants in such complicated reactions cannot give us an insight into their mechanism, since it is impossible to determine the part that the several different processes involved play in the final results. Indeed, Burke and Donnan[1] were unable to explain the variations in the values of K and state "in particular the assumption that it is the silver ions, which take part in the fundamental reaction which regulates the speed, does not appear to offer a simple explanation."

Slator[2] has examined the action of alkyl halides on metallic thiosulphates and considers that he has obtained experimental evidence to show that in this reaction the anions of the salt react with undissociated halide. It is a well-known fact that alkyl halides react only with considerable difficulty on neutral salts of the alkali group, while in salts showing an alkaline reaction the reaction takes place the more readily, the more

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[1] J. Chem. Soc., **85**, 588. It is evident that in such a mixed reaction the relations between the relative reactivity of the alkyl iodides must be different from those obtained in reactions that proceed solely through direct substitution of the halogen, and Burke and Donnan's results show this to be the case. The relations between the above 3 fundamental organic processes and the structures of organic radicals united with the halogen have been partially developed (Michael: J. prakt. Chem., N. F., **60**, 372–384, 409–420; **68**, 499. Ber. d. chem. Ges., **34**, 4215; **42**, 3174, footnote), and the writer will take the occasion of publishing experimental work on the relation of chemical structure to real substitution, and to that of apparent substitution, through elimination and addition to the unsaturated substance thus formed, to develop more fully the theoretical aspect of this very important subject.

[2] J. Chem. Soc., **85**, 1286; **87**, 481.

free *chemical* energy is contained in the metal. Notwithstanding that sodium thiosulphate is a neutral salt, Bunte[1] found that, when it is heated in aqueous solution with so comparatively inert a halide as ethyl bromide, the sodium joined to sulphur is extremely easily replaced by ethyl. Slator found, in the action of ethyl bromacetate on sodium thiosulphate, that with the sodium salt the reaction proceeds very readily, but the addition of small quantities of silver nitrate to the mixture decreases the reactivity to an extent corresponding to the formation of a complex salt, $Na_3Ag(S_2O_3)_2$,[2] which shows a reactivity so small as to be negligible in comparison with that of sodium thiosulphate. Slator[3] believes that the above "complex salt is partially dissociated according to the equation

$$Na_3Ag(S_2O_3)_2 \rightleftarrows Na_2S_2O_3 + NaAgS_2O_3,$$
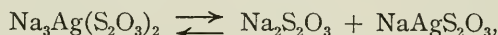
and that the reaction depends on the presence of a small quantity of uncombined sodium thiosulphate."[3] He also believes that "the ions $Ag(S_2O_3)'''$, AgS_2O_3', and the corresponding undissociated salts either do not react or react with only a relatively much smaller velocity, and sees in the fact that addition of silver nitrate to sodium thiosulphate lowers the reactivity so decidedly "strong evidence in support of the view that the reaction is primarily connected with the S_2O_3'' ion."

Slator's experimental results with the thiosulphates show an order of reactivity exactly the reverse of that of the sodium and silver salts of all acids not containing the metal joined directly to sulphur, since, with such salts, it is the silver that reacts with far greater velocity than the somewhat more ionized sodium salt. It is, therefore, obviously wrong to assume the reaction is ionic with the thiosulphate, and we must seek another explanation for the apparently abnormal reactivity of these salts.

In the first paper[4] on the "addition theory," attention was

[1] Ber. d. chem. Ges., **7**, 646.
[2] Such a salt has not been isolated. The salt $NaAgS_2O_3$ dissolves in sodium thiosulphate to form the compound $Ag_2S_2O_3.2Na_2S_2O_3$. The latter salt is quite stable and as its formation proceeds with loss of free *chemical* energy, it should show a smaller reactivity towards alkyl halide than sodium thiosulphate.
[3] J. Chem. Soc., **87**, 490.
[4] J. prakt. Chem., N. F., **37**, 508–511.

directed to the instantaneous and violent addition of methyl iodide to methyl sulphide; it was pointed out that if sulphur in an organic compound exists in a similar condition of "polarity" (it was then called "positive" sulphur) it should also show an additive power for alkyl halide, more or less developed according to its condition of positivity, and should lead to the formation of unstable, metallic sulphinium derivatives. Thus the reaction between methyl iodide and sodium thiocyanate was represented[1] by the equation

$$\text{Na—S—CN} + \text{CH}_3\text{I} = \text{Na—S}\overset{\overset{\displaystyle I \quad CH_3}{\diagdown\diagup}}{—}\text{CN} = \text{CH}_3\text{—S—CN} + \text{NaI}.$$
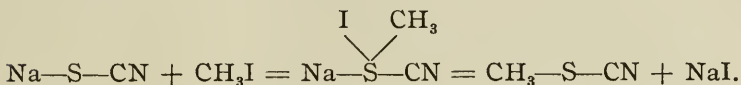
Although thiocyanic acid must have a very considerable affinity constant, its alkali salts react with alkyl halides with great readiness, while the silver salt is comparatively inert.[2] Here we have the same relations as Slator found with the corresponding thiosulphates. Silver is very weakly positive $(\text{AgOH} = 1 \times 10^{-4})$ in comparison with an alkali metal; by replacing the strongly positive sodium by the weakly positive silver, the sulphur in the thiocyanate and thiosulphate loses its additive power for alkyl halide. The reaction, therefore, proceeds by direct substitution of the silver, which, although it goes much faster than the direct substitution of sodium, is considerably slower than the addition process. Slator proved that the reactivity of thiosulphates does not vary greatly when very positive metals, *i. e.*, potassium, sodium, barium or strontium, are present in the salts and that such solutions in reacting with organic halides follow the law of mass action. His assumption that these reactions proceed through union of the anions of the salts with the halides stands in direct contradiction to the properties of these and similar compounds, whereas the chemical explanation just given is in agreement and explains, in a satisfactory manner, the effect of adding silver nitrate.

Senter[3] has published an interesting investigation on the

[1] J. prakt. Chem., N. F., **37**, 509.
[2] Von Meyer: Ann. Chem. (Liebig), **171**, 47.
[3] J. Chem. Soc., **91**, 460.

hydrolytic decomposition of chloracetic acid by water, and of its sodium salt by water and by caustic alkali, as well as on the influence of neutral salts on the velocity constants of these reactions. The reaction velocity of the system, acid and water, is but little affected by neutral salts, or by hydrochloric acid, which leads Senter to the conclusion that it is the undissociated acid that mainly undergoes decomposition. With sodium chloracetate and water, Senter finds that in very dilute solutions the velocity is proportional to the concentration, while it increases more rapidly than the concentration in stronger solutions; sodium chloride exerts a considerable effect, but potassium chloride and nitrate only a slight, negligible, retarding influence. The change with concentration agrees with the assumption that the undissociated salt is acted on, but this view is incompatible with the strictly monomolecular character of this change in very dilute solutions and Senter[1] thinks his experimental results are best explained by assuming the main reaction in dilute solution to take place between $CH_2Cl.COO'$ ions and nonionized water, while in more concentrated solutions the reaction of the undissociated sodium salt becomes of importance. Senter[2] explains the results obtained from sodium chloracetate and alkali by a similar assumption, only here the hydroxyl ions enter into the reaction. He also finds that sodium chloracetate is hydrolyzed only ten times more rapidly by 0.1 N sodium hydroxide than by water, and that the addition of neutral salts to the acetate-alkali system accelerates the velocity constant. These results are, as Senter[3] observed, in striking contrast to those obtained in other systems; thus, in the hydrolysis of esters, the reaction is enormously accelerated by alkali, and the addition of neutral salts decreases the constants. It is evident that results which show evidence of electrolytes reacting in an undissociated condition in aqueous solution, or, in that or a dissociated condition varying with the dilution, and which in part are so contradictory to the ionic point of view, do not

[1] J. Chem. Soc., **91,** 471.
[2] *Ibid.*, **95,** 1828.
[3] *Ibid.*, **91,** 474.

justify Acree[1] in claiming them as a support to the hypothesis that alkylations proceed under all conditions through union of the anions with the organic halide. Senter assumes that water, or alkali, acts on sodium chloracetate by directly replacing the halogen by hydroxyl. The fact that dry sodium chloracetate is decomposed at a moderate heat into glycolide and sodium chloride[2] indicates the existence of a decided affinity between the halogen and the metal. Owing to the resistance connected with the formation of a four-ring, *i. e.*, the β-lactone, the reaction proceeds through interaction of two molecules, forming in glycolide a six-ring derivative.[3] But if this affinity between metal and halogen comes into play in the presence of water, with its assistance the direct, intramolecular formation of sodium chloride is not only possible, but would probably proceed easily, as under such conditions glycollic acid may be formed:

$$\begin{array}{ccccc} \text{Cl} & \!\!\long!\!\!\text{CH}_2 & \longleftarrow & \text{OH} & \text{CH}_2\text{OH} \\ \downarrow & | & & | & = & | & + \text{NaCl.} \\ \text{NaO} & \!\!\long!\!\!\text{CO} & \longleftarrow & \text{H} & \text{COOH} \end{array}$$
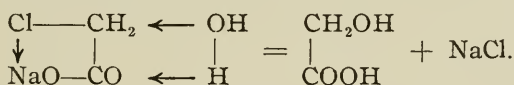
It follows from this interpretation that the more highly ionized the salt is, *i. e.*, the more dilute the solution, the larger must be the proportion of the chemical change that takes place in the $ClCH_2\text{-}COO'$ ions; the comparatively slight increase in the reaction velocity by addition of caustic alkali is also consonant with it. It is probable, however, that, even in undissociated sodium chloracetate the direct replacement of halogen by hydroxyl proceeds, to a certain extent, simultaneously with the process just described and that the relative proportion between the two processes increases in favor of the first, when alkali instead of water is employed.

Euler[4] has examined the reaction between silver nitrate and chloracetic acid, and its salts, and that between silver

[1] Ber. d. chem. Ges., **41**, 3210.

[2] Kekulé: Ann. Chem. (Liebig), **106**, 288. Norton and Tscherniak: Bull. Soc. Chim., **30**, 102. Polyglycolide was formed, but as Bischoff and Walden (Ann. Chem. (Liebig), **279**, 46) subsequently showed that glycolide is formed by heating sodium bromacetate *in vacuo* and that it goes over on heating into polyglycolides, it seems probable that the latter is always the primary product.

[3] Michael: J. prakt. Chem., N. F., **60**, 336.

[4] Ber. d. chem. Ges., **39**, 2726.

nitrate and ethyl bromide. The velocity constant of chlor-
acetic acid and silver nitrate is the same in 45 per cent. alco-
hol as in water. Euler[1] considers this result surprising, since
the dissociation values differ considerably in these solvents;
it is indeed difficult to reconcile the result with the view that
the reaction is ionic. The velocity constant for sodium chlor-
acetate and silver nitrate is much greater than when the free
acid instead of the salt is used, while that with ethyl chlorace-
tate is only one-half of that with the free acid. Euler assumes
that the reaction between chloracetic acid and silver nitrate
is represented by the equation

$$ClCH_2.COOH + AgONO_2 + H_2O =$$
$$HOCH_2.COOH + AgCl + HONO_2,$$
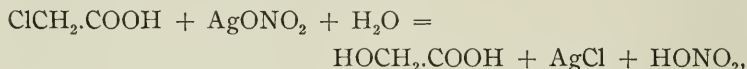
and believes his results are best explained by supposing that in
this, and in similar reactions, where one of the substances is
largely in an ionic condition, the substitution proceeds through
a complex ion of the type $\overset{+}{Ag}.BrC_2H_5$. He thus explains
the decrease in velocity when chloracetic ester instead of the
free acid is used and its increase by using the sodium salt in-
stead of the latter substance.

The first chemical change that takes place in an aqueous
solution of chloracetic acid and silver nitrate is the formation
of a certain quantity of silver chloracetate and nitric acid
and the amount of the organic silver salt must stand in a re-
lation to the acidity constants of chloracetic and nitric acids.
It is a characteristic property of silver salts of organic halogen
fatty acids to decompose extremely easily into silver halide
and organic products, corresponding to the nature of the
acid used.

The decomposition of silver chloracetate was first studied
by Beckurts and Otto,[2] who found that in concentrated solu-
tion silver chloride and glycollic acid are very readily formed,
and that the velocity of this reaction decreases with dilution.
In striking contrast to this instability of the silver salt is the

[1] Ber. d. chem. Ges., **39**, 2729.

[2] *Ibid.*, **14**, 576. The dry silver salt decomposed at about 70° into silver chloride
and glycolide.

comparative great stability of the corresponding sodium derivative,[1] and as the latter salt is undoubtedly dissociated in solution to a greater extent than the former, it would seem as if the dominating factor on which the instability of the silver salt depends can hardly be the formation of chloracetic ions. If the silver chloracetate formed on mixing chloracetic acid and silver nitrate decomposes much faster intramolecularly, *i. e.*, through direct union of the halogen with the metal, than the change represented by the above equation—and this can hardly be doubted—then the decomposition will proceed more or less completely in the first named manner. From this point of view, the use of sodium chloracetate, instead of the free acid, with silver nitrate must increase the reaction velocity enormously as the concentration of the silver chloracetate is greatly increased by the change. Euler's explanation of the decrease ensuing when the ester, instead of acid, is used is open to grave objections; it is not known whether chloracetic ester is capable of forming chloracetic ions at all, and, if so, their concentration must be inconsiderable in comparison with that of the free acid, whereas the velocity is only decreased one-half. According to the above point of view, silver chloracetate can be formed only indirectly from the ester, *i. e.*, from the acid formed through hydrolysis; it is likely, however, that the reaction proceeds partially in this way and partially by direct substitution of the halogen.

The interesting observation of Beckurts and Otto that the stability of silver chloracetate is greater in dilute than in concentrated solution, was made the subject of a quantitative investigation by Kastle.[2] This chemist found, for instance, that, at 100°, in a 0.09 N solution, 43 per cent. was decomposed in one hour, while with a 0.00015 N solution only 3 per cent. was decomposed. Ostwald[3] remarked, regarding the results, that they afford evidence of an intramolecular decomposition,

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[1] Quantitative data with bromacetic acid are given in Senter's recent paper (J. Chem. Soc., **95**, 1835). In 0.1 N solutions the velocity for bromacetic acid and silver nitrate is 63 times greater than that for sodium bromacetate. For silver bromacetate the difference should be still greater.

[2] This Journal, **14**, 586.

[3] Z. physik. Chem., **11**, 431.

since increasing dissociation develops greater stability, which agreed with the view advocated here. Euler's conclusions are based on imperfect assumptions regarding the manner in which the reactions proceed, and all chemical evidence agrees much better with the conclusion that the reactions involved represent not ionic but molecular changes.[1]

Finally, Acree[2] finds confirmation of the view that alkylation reactions proceed by union of the anions of the salt with the alkyl halide in the investigations of Hecht, Conrad and Brückner[3] on the formation of ethers from alcoholates and alkyl halides. These reactions were discussed from the ionic standpoint by Steger,[4] and later very thoroughly by Burke and Donnan,[5] who observe that "the explanation of these anomalies proposed by Steger, based on assumptions concerning the ionization of the sodium alkyl oxide and alkyl iodide in alcoholic solution, does not appear to hold good if the ordinary law of equilibrium is assumed."[6] The writer does not believe that the above researches permit of any legitimate conclusions being drawn with regard to the mechanism of these reactions. How complicated, and how little adapted this physico-chemical method is to throw light on the subject is evident from a research by de Bruyn and Steger,[7]

[1] Acree (THIS JOURNAL, **39**, 243) has criticized Euler's view on the ground that addition of potassium iodide to a solution of caustic potash and ethyl iodide should cause an increase in the concentration of the complex cations, C_2H_5I, $\overset{+}{K}$, and therefore increase the velocity constant of the reaction. Acree and Shadinger (*Ibid.*, **39**, 256) showed, however, that potassium iodide causes a decrease in the constant. Euler used C_2H_5I,$\overset{+}{Ag}$ as a symbol for a chemical type and confirms (Ber. d. chem. Ges., **39**, 2726) Schwab's previous observation, that addition of sodium chloride increases the velocity constant of caustic soda and sodium chloracetate. Are we to suppose from these results that the first reaction proceeds according to Acree's, and the latter according to Euler's views? In view of the irregularity in the results obtained by addition of neutral salts to systems containing organic halides and of the fact that the reason why they are sometimes inert, and sometimes exert an influence in one or the other direction, is so little understood, it is indeed surprising that results obtained by this method should be used as a basis for theorizing on the mechanism of organic reactions.

[2] Ber. d. chem. Ges., **41**, 3210.

[3] Z. physik. Chem., **4**, 273, 631; **5**, 289.

[4] Rec. Trav. Chim., **18**, 13.

[5] J. Chem. Soc., **85**, 581.

[6] *Ibid.*, 588.

[7] Z. physik. Chem., **49**, 336. See Tymstra Bz.: *Ibid.*, 346.

who have shown that addition of water to alcoholic solutions of the following systems,

I. $C_2H_5ONa + CH_3I$,

    II. $CH_3ONa + CH_3I$,

        III. $CH_3ONa + C_2H_5I$,

           IV. $C_2H_5ONa + C_2H_5I$,
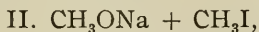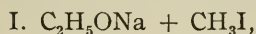
effects a decrease of the velocity constant in I; an increase up to 30 per cent. water, and above that a decrease, in II; a regular decrease in III; and a decrease up to 30 per cent. water, and then no further change, in IV. Here we have four systems which, chemically, are strictly analogous; if the reactions are ionic the addition of water should increase dissociation and consequently the velocity of reactions in each case. Yet the influence of water is different in each of the four systems, and in none of them does it conform to the requirements of the ionic theory. Until these anomalies are satisfactorily explained, it is a travesty on science to indulge in speculations about the mechanism of these reactions from the ionic point of view.

The writer has entered, in some detail, into the application of certain physical-chemical methods, which have been used with success in the examination of dilute solutions of inorganic electrolytes, to organic reactions, where at least one of the constituents is practically a nonelectrolyte, in the belief that the time has come to protest against the reckless theorizing on results obtained by these methods in which some enthusiastic followers of the ionic hypothesis have indulged as well as against their indifference to the results obtained in other ways and the ignoring by them of the chemical aspects of the problems. In the following statement regarding physical-chemical organic research, the writer, at all events, agrees with Acree:[1] ''The worker who would do great service in this branch of science must have *as the great essential* such a broad and deep knowledge of organic chemistry that he can recognize wrong interpretations of reaction mechanisms almost by intuition; he must not make wrong postulations

[1] Science, **30,** 625 (1909).

regarding reactions." It would seem as if, in the researches discussed in this paper, Acree has not been altogether successful in his endeavors to realize these admirable ideals; for imperfect and incorrect representations of the views and results of other chemists certainly do not indicate "a broad and deep knowledge." Acree's own interpretations of reaction mechanisms, and some of those he favors, are plainly untenable, and there is no lack of "wrong postulations." The results obtained by him in the alkylation of urazole derivatives show that these reactions proceed in conformity with the law of mass action, *but do not warrant any of his conclusions regarding the mechanism of these, or of other reactions of tautomeric substances, nor do they stand in opposition to the "addition theory," but are further evidence in its favor, and of the necessity of founding the theory of organic chemistry on the law of entropy.*

ON THE REACTIONS OF DIAZOALKYLS WITH 1-PHENYL-2-METHYLURAZOLE.

[FIFTEENTH COMMUNICATION ON URAZOLES.]

By SIDNEY NIRDLINGER AND S. F. ACREE.

The efforts to find the exact position of the two acid hydrogen atoms of phenylurazole[1] have shown that this compound is to be classed, from a theoretical point of view, among the most interesting and important of all tautomeric substances. The presence of two movable hydrogen atoms and the consequent possibilities of obtaining a large number of isomeric derivatives, each of which can be estimated quantitatively under easily regulated conditions, has made possible a quantitative study of the tautomeric phenomena presented, and the results have an important bearing on the question of tautomerism in general.

From a quantitative study of the reactions of the salts of phenylurazole, phenyl-4-methylurazole, and phenyl-3-thio-

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[1] THIS JOURNAL, **27**, 118; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1; **39**, 125. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

urazole, in all of which it has been shown by Acree and Brunel[1] that there are probably two or more tautomeric forms whose equilibrium constants are established practically instantaneously under the conditions maintained in the work, Acree[2] and his collaborators have been able to show that the results are not in harmony with the theories of Comstock,[3] Wheeler,[4] Nef,[5] and Michael,[6] but are in accordance with the theory proposed by Acree,[7] namely, that *in all cases in which these tautomeric urazoles give two or more stable isomeric products as the result of a reaction, they do so because they exist in two or more forms in equilibrium, each of which reacts independently, or because one form is changed into stable derivatives through two or more side reactions.* The ratio of the products obtained depends entirely on the equilibrium conditions and the several reaction velocities. The mathematical treatment of this theory has been worked out in detail for the most part[8] and all the experimental results are in harmony with what the theory demands. This theory is not being followed blindly, however; it is used as a working hypothesis and is being subjected to the same rigid scrutiny that was applied to the others. It will be discarded as soon as it has outlived the "day of usefulness" that is the glory of man or theory.

Since, however, all the work up to the present has been done on the metallic salts, it seemed desirable to study the reactions of the urazole acids themselves, the compounds chosen being those that under the conditions studied established the equilibrium practically instantaneously.

This report is confined to the reactions of the diazoalkyls with the urazole acids. The diazoalkyls were chosen as the alkylating agents because (1) they all, with the very important exception of diazopropylene, $CH_2 = CH—CH = N_2$, react *very rapidly* with the urazole acids, and because (2) they yield

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[1] Brunel: Diss., Johns Hopkins Univ., 1906.
[2] This Journal, **38**, 1; **39**, 125, 226. Ber. d. chem. Ges., **41**, 3199.
[3] Ber. d. chem. Ges., **23**, 2274. This Journal, **12**, 493; **13**, 514, 525.
[4] This Journal, **21**, 187; **23**, 135; **30**, 28.
[5] Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83, etc.
[6] J. prakt. Chem., [2] **37**, 469; **45**, 580; **46**, 189; etc.
[7] *Loc. cit.*
[8] This Journal, **38**, 1.

a mixture of isomeric esters which can be worked with quantitatively. *It was believed that this would give us a new method for studying the question whether the salts of urazoles have equilibrium constants different from those of the acids, and Mr. E. K. Marshall has now shown that such differences really exist.* As was predicted, these differences are too small to be measured easily by conductivity methods. The diazoalkyl reacts with the urazole acid liberated from the salt by the action of acids, water, alcohol, etc., before it changes into the equilibrium condition, a change that is too small and too rapid to be followed by conductivity measurements.

The salts, when treated with an alkylating agent, have all given a constant ratio of esters in any given series of experiments, but it does not follow that this would be true for the acids.[1] If we consider the following scheme,

$$\begin{array}{ccc}
\mathrm{C_6H_5-N-NCH_3} & \mathrm{C_6H_5N-NCH_3} & \mathrm{C_6H_5N-NCH_3} \\
\mathrm{O:C \quad C:O} \rightleftharpoons & \mathrm{O:C \quad C:O} + \underset{+\ CH_2N_2}{\overset{+\ K_{trans}}{H \longrightarrow}} & \mathrm{O:C \quad C:O} \\
\mathrm{NH} & \mathrm{N} & \mathrm{NCH_3}
\end{array}$$

$$\mathrm{K_3} \updownarrow$$

$$\begin{array}{ccc}
\mathrm{C_6H_5N-NCH_3} & \mathrm{C_6H_5-N-NCH_3} & \mathrm{C_6H_5N-NCH_3} \\
\mathrm{HOC \quad C:O} \rightleftharpoons & \mathrm{\overline{O}C \quad C:O} + \underset{K'_{trans}}{\overset{+}{H} \longrightarrow} CH_3\mathrm{OC} \quad \mathrm{C:O}, \\
\mathrm{N} & \mathrm{N} & \mathrm{N}
\end{array}$$
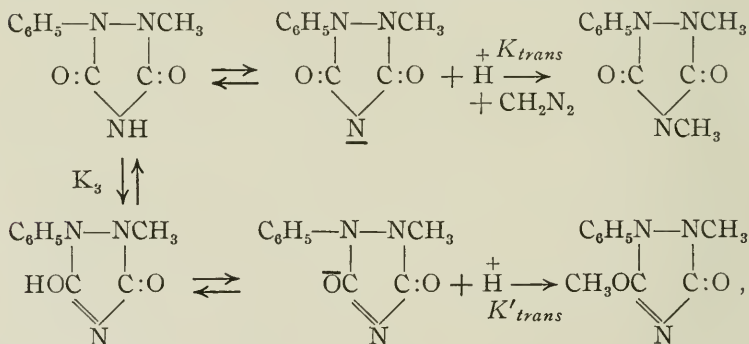
[1] Acree showed that 1-phenyl-2-methylurazole and 1-phenyl-4-methylurazole yield with diazomethane *stable* isomeric N-esters and O-esters. This proves that these urazoles must exist either (A) in only one tautomeric form which reacts with the diazomethane in two (or more) independent side reactions, or (B) in two or more tautomeric forms; in this case (1) each form may react independently with the diazomethane and yield its corresponding ester, or two (or more) esters by side reactions, or (2) one form alone may yield the two esters by side reactions. The probability of (A) can be eliminated by the following evidence: The salts of 1-phenyl-2-methylurazole and 1-phenyl-4-methylurazole exist in two tautomeric forms and the two acids are liberated when a strong mineral acid is added. But it might be thought that one of these tautomeric acids immediately changes into the other and that the acid actually isolated and worked with exists in only one form. But the urazole acids are themselves also weak bases; either tautomeric form of the acid would therefore form a salt with other molecules of itself, which salt would partially rearrange into the other tautomeric salt. Both tautomeric salts are constantly being hydrolyzed, alcoholyzed, etc., into the corresponding two tautomeric acids, which are therefore generally in solution together. Traces of alkalies from glass, etc., could also bring

we readily see that the constancy of ratio between the isomeric esters is only a special case, due either to the fact (1) that the constants for the velocity of establishment of K_3, which is the equilibrium ratio between the molecular enol and keto forms, are very large in comparison with K_{trans}, the velocity constant for the reaction of the keto form with the diazo compound, and K'_{trans}, the corresponding constant for the enol form; or to the fact (2) that, if the constants for the velocity of establishment of K_3 are very small, K'_3, the ratio of the molecular enol and keto forms at the particular time t in question, is approximately equal to $\dfrac{K_{trans}}{K'_{trans}}$. In K_{trans} and K'_{trans} no consideration is taken of the fact that the acid is ionized or that the reaction may either be ionic or molecular, or both. If α is the percentage of ionization of the keto form of the acid and the reaction is ionic we would have $K_{trans} = \alpha K_{1\,trans}$, in which $K_{1\,trans}$ is the real reaction constant.[1] In any case K_{trans} and K'_{trans} are equal to the real reaction constants multiplied by their corresponding factors, the ratio of which factors probably does not change appreciably during the reaction periods measured.

In every other case we would expect the ratio of esters to be dependent on the time. For we have $\dfrac{c}{c'} = K'_3$ at the time t, and

$$\frac{dc_2}{dt} = \frac{K_{trans}K'_3}{1 + K'_3}\,(c + c_1 - c_2 - c_3)^2, \text{ and}$$

$$\frac{dc_3}{dt} = \frac{K'_{trans}}{1 + K'_3}\,(c + c_1 - c_2 - c_3)^2,$$

in which c is the concentration of the practically undissociated keto acid present, c_1 the concentration of the enol acid, c_2 the concentration of the keto ester formed, and c_3 that of the

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about such tautomeric changes. We believe that each form of the acid yields (1) the corresponding ester, and not (2) two isomeric esters through side reactions; but we are testing this latter possibility experimentally and practically all of the conclusions arrived at in the following pages can be deduced as readily from one point of view as from the other. We therefore use the former (1) in the following pages for the sake of clearness and convenience, believing it to be nearest the truth.

[1] Ber. d. chem. Ges., **41**, 3212.

enol ester. When equimolecular amounts of acid and diazo-
alkyl are used, the concentration of the latter is also expressed
by $(c + c_1 — c_2 — c_3)$. Dividing and integrating, we ob-
tain, if c_2 and c_3 are zero when $t = 0$,

$$\frac{c_2}{c_3} = \frac{K'_3 K_{trans}}{K'_{trans}}.$$

But if K'_3 is a function of the time, t, then the ratio $\frac{c_2}{c_3}$ would
vary accordingly. The reactions between the urazole salts
mentioned above and the alkyl halides show most conclusively
that the time function of K'_3 need not be considered in the
case of these salts. The salts, however, are very different
from the acids, being highly ionized and comparable in every
way with the salts of strong acids, while the acids themselves
are very little ionized,[1] and far less reactive towards alkyl
halides. Thus, since the urazole acids react so exceedingly
rapidly with diazoalkyl,[2] we might expect different results
from some of the urazole acids[3] and then we might get some
clue as to the rapidity of establishment of K_3 or its value.

If K'_3 changed very slowly in comparison with the rate of
alkylation, then the addition of a small fraction of a molecu-
lar equivalent of diazomethane would give a ratio of esters
approximately equal to $\frac{cK_{trans}}{c_1 K'_{trans}}$, while the addition of a molec-
ular equivalent would give a ratio approximating K'_3. The
addition of different amounts of diazomethane would give a
variable ratio, then, unless $K_{trans} = K'_{trans}$, or, in other words,
$\frac{c_2}{c_3} = K'_3$.[4] This last possibility can be eliminated by using
other diazoalkyls such as diazoethane, -propane, -butane, etc.,
which give different values of $\frac{c_2}{c_3}$, which would then not be
equal to K'_3. On the other hand, if K'_3 is not a function of

[1] This Journal, **39**, 126.

[2] Ber. d. chem Ges., **27**, 1889.

[3] We have now found this to be the case with the tautomeric 1-phenyl-3-oxy-4-
phenyl-5-thiolurazole and 1-phenyl-3-hydroxy-4-phenyl-5-thionurazole which change
into each other slowly. Dr. Nirdlinger's results will appear soon, and those of Mr.
E. P. Doetsch later.

[4] This Journal, **38**, 7.

t, when compared with K_{trans} and K'_{trans}, we should expect a constant ratio of esters as in the case of the salts. The experimental evidence shows conclusively that we do get a constant ratio of esters for variable amounts of diazoalkyl used. We must conclude, therefore, that however rapidly the diazoalkyls act with 1-phenyl-2-methylurazole, the various equilibrium constants are established very much more rapidly. Mr. E. K. Marshall is studying these reactions at low temperatures to see if the changes take place slowly enough to be measured under those conditions.

Owing to the fact that the diazoalkyls are decomposed so rapidly by water,[1] it was impossible to use aqueous solutions in studying these reactions. It was hoped that aqueous solutions could be used because Acree and Shadinger[2] have determined the affinity constants of a number of these urazoles in water. An attempt was made to suspend the 1-phenyl-2-methylurazole in water and add a ligroin solution of diazomethane, but only a few milligrams of ester were obtained. The amount was too small to analyze and besides it may have been formed from the small amount of the acid which was dissolved by the ligroin. With an ether solution of diazomethane and an aqueous solution of the urazole acid no better results were obtained. This difficulty with the aqueous solutions, combined with the extreme rapidity of the reaction, made an exact study of its mechanism impossible, but still we have some clues as to its general nature. *Whatever the nature of the reaction between the diazoalkyl and one of the tautomeric forms of the acid, the reaction between it and the other form must be of the same* APPARENT[3] *order.* Otherwise we would not get a constant ratio of esters for variable amounts

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[1] von Pechmann: Ber. d. chem. Ges., **27**, 1889.

[2] THIS JOURNAL, **39**, 124.

[3] The possibility that one ester is formed by a bimolecular reaction, for example, and the other ester from the same or another tautomeric form of the acid by a far more complicated but apparently bimolecular reaction, as Julius Meyer (Z. physik. Chem., **66**, 81; **67**, 257) has found in other very interesting cases, seems to be excluded by the fact that *all* diazoalkyls yield ratios of esters which do not vary with different concentrations and different time periods. It would be in only one case in a very large number that *even two* diazoalkyls could behave in such a way, as a large number of constants would be involved in the two sets of reactions yielding the two esters. The two sets of reactions are therefore probably very similar.

of alkylating agent used. For while the theory of side reactions of the same order requires that the ratio of products during any one reaction be constant, no matter what the order of the reactions,[1] since it depends solely on the ratio of the velocity constants, at the same time, even if K'_3 is constant, a changing ratio of products will be obtained when the two reactions are of a different order, since the rates of formation of the two esters will not be changed in the same way. If, for example, the keto ester is formed by a bimolecular reaction and the enol ester by the following trimolecular reaction between the urazole acid and the diazoalkyl, the concentration of which at any moment is designated by $(A - c_2 - c_3)$, we have

$$\frac{dc_2}{dt} = \frac{K_{trans} K_3}{1 + K'_3} (c + c_1 - c_2 - c_3)(A - c_2 - c_3),$$

$$\frac{dc_3}{dt} = \frac{K'_{trans}}{1 + K'_3} (c + c_1 - c_2 - c_3)(A - c_2 - c_3)^2, \text{ and}$$

$$\frac{dc_2}{dc_3} = \frac{K_{trans} K'_3}{K'_{trans}} \cdot \frac{1}{(A - c_2 - c_3)}.$$

On integrating the last equation we would get an expression involving $(A - c_2 - c_3)$. Since K'_3 is a constant the ratio $\frac{c_2}{c_3}$ would then depend on $(A - c_2 - c_3)$ or the concentration of the diazoalkyl, which is a function of t, and $\frac{c_2}{c_3}$ would therefore vary with t. Since we get a constant ratio of esters from those diazoalkyls which react very rapidly, as well as from diazopropylene, which reacts very slowly, we know that the two reactions are of the same apparent order.

There is no experimental evidence from this work as to whether the diazoalkyls form intermediate complex anions or cations. It seems probable that diazomethane is basic in character and would form the complex cation $CH_2N_2\overset{+}{H}$. These complex ions might react with the urazole ions or the urazole molecules; very little is really known about this reaction. It follows from equations (1) and (2), on pages 365, 366,

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[1] Acree: THIS JOURNAL, **38**, 1–8. Wegscheider: Z. physik. Chem., **30**, 593.

that $\dfrac{C_{ei}}{C_{ki}} = K\dfrac{C_{e\,mol.}}{C_{k\,mol.}}$. In acid solutions, therefore, there is *always* practically a constant ratio of the ions and also of the molecules of the two tautomeric forms, and the fact that a constant ratio of esters is obtained, even when, as shown by Mr. Marshall, hydrochloric acid is added, does not give any evidence as to whether the ions or the undissociated molecules yield the esters. In the case of diazoacetic ester, which reacts thus,

$$\text{ROOCCH} = N_2 + \overset{+}{H} + \overset{-}{Cl} + (H + OH) \text{ or } H_2O$$
$$\longrightarrow \text{ROOCCH}_2\text{OH} + \overset{+}{H} + \overset{-}{Cl} + N_2,$$
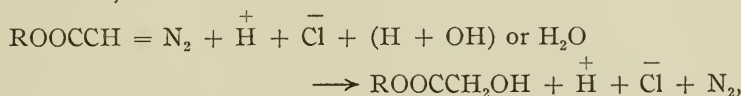
the velocity is dependent upon the concentration of the hydrogen ions and is, according to Bredig and Fraenkel, therefore due to intermediate complex salt and ion formation.[1] Our reactions may or may not be similar, and we shall study the reactions of these urazoles with diazoacetic esters.

This problem also permits us to study the question of abnormal hydrolysis of salts of tautomeric compounds.[2] The hydrolysis of the salts of strong bases and weak acids is expressed by the equation $K_{hyd} = \dfrac{K_w}{K_{affur}}$, in which K_{hyd} is the hydrolysis constant, K_w the ion product of water, and K_{affur} the affinity constant of the urazole acid. But if there are two tautomeric salts in equilibrium, the affinity constant of the acid is not a simple number and is dependent on the affinity constant of the keto form and on that of the enol form, or other reacting form, whatever its nature, both of which are formed by the hydrolysis of the corresponding salts. Taking the scheme on page 360, we see that the affinity constant of the keto form is

$$K_{affk} = \frac{(C_{ki} \times H)(1 + K_3)}{K_3 \times C_{ur}} \tag{1},$$

that of the enol form

[1] Ber. d. chem. Ges., **40**, 4015. Bredig: Chemische Kinetik des Diazoessigesters und ihre Anwendungen: Z. physik. Chem., **60**, 202.

[2] Ber. d. chem. Ges., **35**, 210; **39**, 2098; **37**, 2298, 2468; **39**, 1607, 2265. Z. physik. Chem., **47**, 618. For a fuller discussion see Acree: This JOURNAL, **38**, 30–41.

$$K_{affe} = \frac{(C_{ei} \times H)(1 + K_3)}{C_{ur}} \qquad (2),$$

and that of the total acid

$$K_{affur} = \frac{(C_{ki} + C_{ei}) \times H}{C_{ur}} = \frac{K_{affe} + K_3 K_{affk}}{1 + K_3} \qquad (3),$$

in which K_{affk} is the affinity constant of the keto form, K_{affe} that of the enol form, K_{affur} that of the total acid, C_{ki} the concentration of the keto ions, C_{ei} that of the enol ions, and H that of the hydrogen ions. C_{ur} is the concentration of the molecular urazole acid, and K_3 has the usual significance. But if the affinity constants of the two forms are different, anything that will disturb K_3 will change the value of K_{affur}. We would then get a new value, K'_{hyd}, for the hydrolysis constant, which would be equal to $\dfrac{K_w}{K'_{affur}}$, in which K'_{affur} is the new affinity constant of the urazole acid. This could be brought about in certain cases by adding a salt which would not only have a different equilibrium constant, K'_3,[1] but would also introduce a new ratio $C'_{ki} : C'_{ei}$ into the solution. Now we have proved, by the application of the mass law to such a case, that all salts must have a constant ratio of the concentrations of the two anions; namely, that for the acid itself, $C_{ki} : C_{ei}$. Notwithstanding this our experimental results *seem* to indicate that the addition of such a salt changes $C_{ki} : C_{ei}$ and hence K_3. If this is true it may take place because the ordinary formula for the mass law does not hold in the rather concentrated solutions that we use, or because by the addition of the salt we are changing the *medium*, in which the values of K_1, K_2 and K_3, etc., may change. If this is true, then the addition of a diazoalkyl to a solution of 1-phenyl-2-methyl-urazole containing several molecular amounts of the sodium salt should give an abnormal ratio of esters, since not only the value of K_3 but also the ratio of the ionic forms changes. We actually obtain an increase of 5 *per cent.* in the amount of enol ester in the presence of the salt. This proves that there is either an increase in the ratio of the concentration of the

[1] Mr. Marshall and Mr. Doetsch have now shown this to be the case with the tautomeric forms of 1-phenyl-2-methylurazole and 1-phenyl-3-hydroxy-4-phenyl-5-thionurazole.

enol ions to that of the keto ions, or that there is a corresponding change in the ratio of the concentration of the *enol molecular* form to that of the keto molecular form, and these conclusions are beautifully substantiated by Mr. E. K. Marshall's proof that the acid liberated from the sodium salt and alkylated *at once* with diazomethane yields a higher ratio of enol ester to keto ester than does the same acid after it attains its equilibrium. This proves then that there must be a change in the affinity constant of this urazole acid in the presence of its salts—and hence a change in the hydrolysis constant. In the other cases which we are studying, it now appears that some urazole acids will give a *lower* ratio of enol ester to keto ester, and others will hardly have the normal ratio changed, in the presence of the salt. In other words, it seems now that some urazole acids will give a hydrolysis constant which is abnormally high, others a normal hydrolysis constant, and still others an abnormally low hydrolysis constant.

All of the above reactions would necessarily be modified to some extent if the urazole salt causes a catalytic change in the two reaction velocities, or if any other reactions not considered above are found to be taking place. We realize that these reactions may be very complicated and that conclusions can be drawn only tentatively at present. But that the *sodium ions* do not produce this change is shown by the fact that sodium iodide did not cause an appreciable change in the ratio of esters, a difference of only o.3 per cent. being observed. This is far less than the experimental error. We must yet determine whether urazole ions can effect such catalytic changes. The following table shows the results obtained:

20 cc. o.0523 Vol. Normal 1-Phenyl-2-methylurazole in Methyl Alcohol and 30 cc. Ethereal Diazoethane Solution.

	Conc. diazo sol. 0.0087	0.0174	0.0261	0.0348	
	Per cent. *N*-ester in total product.				Average.
1 - Phenyl - 2 - methylurazole	69.0	67.1	68.4	67.5	68.0
1 - Phenyl - 2 - methylurazole and 3 mols. sodium salt	64.0	64.5	62.3	61.1	63.0
1 - Phenyl - 2 - methylurazole and 3 mols. NaI	68.7	67.2	66.6	68.3	67.7

Phenylurazole.—Phenylurazole was prepared according to the method described by Acree.[1] It melted at 261°–264° without decomposition.

1 - Phenyl - 2 - methylurazole. — The 1 - phenyl - 2 - methyl-urazole used in this work was made as follows: Twenty grams of phenylurazole were suspended in 200 cc. of alcohol and the theoretical amount of aqueous potassium hydroxide was added. Then about two molecular amounts of methyl iodide were added and the whole mixture was boiled four hours under a return condenser. The solution was evaporated to remove the alcohol and the excess of methyl iodide, and then acidified and filtered. The precipitate was extracted with chloroform to separate the unchanged phenylurazole, which is insoluble. The chloroform solution was filtered and extracted with alkali, which removes the 1-phenyl-2-methyl- and 1-phenyl-3-methoxyurazole and leaves any di-alkyl derivative in the chloroform. The alkaline extract was acidified and filtered and the precipitate was evaporated with concentrated hydrochloric acid several times to dryness on a water bath to hydrolyze the methoxy ester. Then the phenyl-2-methylurazole was extracted from the insoluble phenylurazole with chloroform, and the solid obtained by evaporating the chloroform was crystallized from alcohol. From 20 grams of phenylurazole 8.5 grams of 1-phenyl-2-methylurazole melting at 185°–186°, 0.5 gram melting at 175°–178° and a residue of 1.5 grams of esterified product were obtained. The unchanged phenylurazole was recovered.

ON SOME 1-PHENYL-2-METHYL-4-ALKYLURAZOLES.

(BY WM. J. HEAPS.)

As the reactions of 1-phenyl-2-methylurazole are being studied extensively in this laboratory, it was thought desirable to make various 4-alkyl derivatives of it in order to characterize them. The 1-phenyl-2-methylurazole used in this work was made in the usual way and melted sharply at 185°.

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[1] THIS JOURNAL. **38,** 56.

1 - Phenyl - 2 - methyl - 4 - ethylurazole. — To 5 grams of dry 1-phenyl-2-methylurazole were added 22.5 cc. of a normal solution of potassium hydroxide and then 60 cc. alcohol and 1.2 molecules of methyl iodide. The mixture was boiled on the water bath under a return condenser for 6 hours, the alcohol evaporated off and the residue evaporated to dryness with hydrochloric acid in order to saponify any *O*-ester present. An excess of alkali was added and the *N*-ester extracted with chloroform and recrystallized from alcohol. It was a white solid soluble in alcohol, ether and chloroform, and melting at 112°. Yield, 2.5 grams.

Hydrolysis.—The ester was hydrolyzed in small tubes with alcoholic hydrochloric acid in the usual way[1] to see if any *O*-ester were present, but only a trace was found mixed with the *N*-ester.

0.1195 gram of ester lost 0.0009 gram, or 0.75 per cent.

Phenyl-2-methyl-4-propylurazole.—This was made from sodium phenyl-2-methylurazole and propyl iodide in the usual way: 2.4 grams of ester melting at 75° were obtained from 5 grams of phenyl-2-methylurazole. The hydrolysis showed the substance to be 99 per cent. pure. Hydrolysis:

0.101 gram of ester lost 0.001 gram, or 1 per cent.

0.1111 gram of ester lost 0.0008 gram, or 0.7 per cent.

Analysis:

0.1764 gram substance gave 0.3997 gram CO_2.

	Calculated for $C_{12}H_{15}O_2N_3$.	Found.
N	61.7	61.8

Phenyl-2-methyl-4-butylurazole.—This was made from sodium phenyl-2-methylurazole and butyl iodide. The ester is a heavy oil and could not be made to solidify, although many different solvents were used. That it was practically freed from the isomeric *O*-ester by the treatment with the alcoholic hydrochloric acid is shown by the following analysis:

Hydrolysis:

0.1143 gram of oil lost 0.0006 gram, or 0.5 per cent.

[1] See page 374.

Phenyl-2-methyl-4-isoamylurazole.—This ester was prepared in the usual way from sodium phenyl-2-methylurazole and isoamyl iodide. Two grams of phenyl-2-methylurazole gave 0.95 gram ester melting at 179°. The ester was soluble in alcohol, ether and chloroform. The treatment with alcoholic hydrochloric acid removed nearly all of the isomeric *O*-ester.

Hydrolysis:

0.1189 gram ester lost 0.0026 gram, or 2 per cent.

ON THE VELOCITY OF ALKYLATION OF THE SODIUM AND SILVER SALTS OF PHENYL-2-METHYLURAZOLE.

It was thought desirable to measure the values of the alkylation constants, and the ratios of esters formed, in the reactions between the salts of 1-phenyl-2-methylurazole and methyl and ethyl iodide, in order to get an indication of its properties and to compare it with 1-phenyl-4-methylurazole.[1] The sodium 1-phenyl-2-methylurazole was made by the method described by Shadinger.[2] The acid suspended in water was carefully neutralized by adding the theoretical amount of acid sodium carbonate and the resulting solution was evaporated on the water bath to dryness, water added and the evaporation to dryness repeated several times. Then the salt was crystallized once from water and dried in an air bath at 115°. It was neutral to phenolphthalein and perfectly white. In making the silver salt the 1-phenyl-2-methylurazole[3] was dissolved in the theoretical amount of potassium hydroxide and one molecular equivalent of silver nitrate was added. The white precipitate formed was filtered off, washed thoroughly with water, then with alcohol and ether, and dried on a porous plate. When pure it was not readily discolored by the light.

The alkylations were carried out as already described.[4] In the case of the silver salt it was impossible to obtain any reaction constants, as the silver iodide seemed to coat the unchanged urazole salt, even when the tubes were shaken con-

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[1] Ber. d. chem. Ges., **41**, 3225–3235.

[2] This Journal, **39**, 132.

[3] *Ibid.*, **38**, 59.

[4] Ber. d. chem. Ges., **41**, 5221.

tinuously during the alkylation. The experiments were carried out at 60°.[1] The constants were calculated by the usual bimolecular equation.

Table I.—0.3 Wt. N Sodium Salt of Phenyl-2-methylurazole and 0.3 Vol. N Methyl Iodide at 60°.[2]

t (hours).	*A*.	Total product.	Per cent. *N*-ester.	*AK*.	$\frac{AK'}{N\text{-deriv.}}$	$\frac{AK''}{O\text{-deriv.}}$
1	0.307	0.1890	96.0	1.6	1.53	0.07
2	0.307	0.2399	98.3	1.8	1.77	0.03
3	0.307	0.2616	95.5	1.9	1.81	0.09
4	0.307	0.2627	....	1.9	....	....

Table II.—0.3 Wt. N Silver Salt of Phenyl-2-methylurazole and 0.3 Vol. N Methyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-deriv.	Per cent. *O*-deriv.
8	0.307	0.0893	51.0	49.0
17.5	0.307	0.0913	52.3	47.7
24	0.307	0.0877	49.5	50.5
28	0.307	0.0935	51.7	48.3

Table III.—0.3 Wt. N Sodium Salt of Phenyl-2-methylurazole and 0.3 Vol. N Ethyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-ester.	*AK*.	$\frac{AK'}{N\text{-deriv.}}$	$\frac{AK''}{O\text{-deriv.}}$
0.5	0.3285	0.0298	(100.1)	0.199	0.199	...
1	0.3285	0.0607	91.0	0.226	0.205	0.021
2	0.3285	0.0848	91.0	0.174	0.158	0.016
3	0.3285	0.1042	95.8	0.154	0.147	0.007
4	0.3285	0.1144	...	0.133	...	...

Table IV.—0.3 Wt. N Silver Salt of Phenyl-2-methylurazole and 0.3 Vol. N Ethyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-deriv.	Per cent. *O*-deriv.
10	0.3285	0.0595	11.1	88.9
17.5	0.3285	0.1168	11.0	89.0
23	0.3285	0.1161	10.1	89.9
48	0.3285	0.0960	13.3	86.7

The 1-phenyl-2,4-dimethylurazole obtained from the experiments with methyl iodide melted sharply at 96°,[3] while

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[1] For description of the bath see Brunel: Diss., Johns Hopkins Univ., 1906.
[2] *Ber. d. chem. Ges.*, **41**, 3231, 3232.
[3] *Ibid.*, **21**, 1223; **35**, 1563. THIS JOURNAL, **38**, 69.

the 1-phenyl-2-methyl-4-ethylurazole melted at 114°.5.[1] From these experiments we see that this sodium salt is less reactive than the sodium salt of 1-phenyl-4-methylurazole.[2] It gives, however, about the same ratio of esters. When we come to the silver salts we find that while with methyl iodide the ratio of esters is about the same, with ethyl iodide the silver phenyl-2-methylurazole gives much more oxygen ester than the corresponding silver 1-phenyl-4-methylurazole under the same conditions.[2] That the salts of 1-phenyl-2-methylurazole are less reactive is what might be expected from the work of Shadinger[3] on the affinity constants of these acids, the salts of the stronger urazole acids having generally higher alkylation velocities. It has therefore been found that the 4,5-urazole group has a greater tendency to give oxygen derivatives than the 2,3-group.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOMETHANE.

The ether used in this work was dried over sodium, the acetone and chloroform over fused calcium chloride and the alcohols over lime, and distilled. Diazomethane was made by the method of von Pechmann.[4] The methylurethane, obtained by the reaction of methylamine on ethyl chlorcarbonate, was treated in ether solution with the gases evolved by the action of nitric acid on arsenious oxide in order to obtain the methylnitrosourethane. According to von Pechmann[5] this substance, as well as the diazomethane, is extremely poisonous. Dr. Nirdlinger found, however, that neither of these substances had any ill effect on the skin, and the diazomethane did not affect his breathing in any way. The alkylations were carried out as follows: One gram of 1-phenyl-2-methylurazole was dissolved in a measuring flask in 100 cc. of the solvent to be used. In the case of ether 0.65 gram was the maximum amount of urazole that could be dissolved. Of this solution 20 cc. were taken for each experiment. The

[1] This Journal, **38**, 76.
[2] *Loc. cit.*
[3] This Journal, **39**, 126.
[4] Ber. d. chem. Ges., **27**, 1888; **28**, 855, 1624; **29**, 2591; **30**, 646.
[5] *Ibid.,* **27**, 1888.

diazomethane solution was made by pipetting 2 cc. of the methylnitrosourethane into a dry 250 cc. flask and adding 30 cc. of dry ether and 2.2 cc. of a 25 per cent. methyl alcohol solution of potassium hydroxide.[1] Then the ether and diazomethane were distilled over into a receiver containing a small amount of ether to absorb the diazomethane gas, which came over very rapidly at first. The diazomethane solution was then made up to 100 cc. Ten cc. of this solution were transferred to a dry extraction funnel and an excess of a standard ethereal iodine solution added. The excess of the iodine was titrated back with sodium thiosulphate solution, starch being used as an indicator. This gave the strength of the diazomethane solution in cc. of iodine.[2] From a curve, prepared on the basis of this, the amount of diazomethane solution equivalent to 0.2 gram 1-phenyl-2-methylurazole was calculated. Then one-fourth of this amount of diazomethane solution was pipetted into a 100 cc. bottle and sufficient ether to make the solution up to 30 cc. was added. In the next bottle one-half, in the next three-quarters, and in the last, one molecular equivalent of the diazo solution was made up to 30 cc. as above. Usually it took from 20 to 22 cc. of the diazo solution for 0.2 gram of 1-phenyl-2-methylurazole. Twenty cc. of the urazole solution described above was run beneath the ether by means of a pipette and the bottles were shaken. The yellow color of the solutions generally disappeared immediately in all of the bottles; but in some cases a slight yellow color remained in the bottle containing equimolecular amounts of the two solutions. The mixed solvents were then evaporated off, the residue was transferred to an extraction funnel by means of chloroform and then extracted several times with alkali to remove the unchanged acid. Finally the chloroform solution was carefully evaporated off below its boiling point in a weighed dish. After the ester had come to constant weight in a vacuum desiccator, it was

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[1] Ber. d. chem. Ges., **28**, 855.

[2] Monats. Chem., **24**, 364. Wegscheider and Gehringer reported that they obtained twice the amount of ester calculated from the iodine used. This does not agree with our experience. Careful experiments have generally shown the ester formed and iodine used to correspond, but there are in some cases apparent discrepancies which we are investigating.

transferred by means of chloroform or ethyl bromide to a small tube drawn out to a capillary at one end. The solvent was then evaporated down to one or two cc. and 5 cc. of a saturated alcoholic hydrochloric acid solution added, and the tube was sealed off. The tube, which had to be handled carefully, was heated 1 hour at 100° and was then cooled and opened. The contents, after being transferred to a separating funnel, were extracted with alkali. This removed the 1-phenyl-2-methylurazole resulting from the hydrolysis of the 1-phenyl-2-methyl-5-methoxyurazole or 1-phenyl-2-methyl-3-methoxyurazole. The chloroform was evaporated off in a weighed dish and the resulting nitrogen ester was weighed. The error of this method is about 3 per cent.[1]

Experiment 1.—20 cc. ether solution containing 0.13 gram of 1-phenyl-2-methylurazole (0.034 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.00568	0.0200	0.0199	(99.5)	(0.5)
0.01136	0.0337	0.0309	91.7	8.3
0.01703	....	....	....	...
0.0227	0.1254	0.1136	90.6	9.4

Experiment 2.—20 cc. chloroform solution containing 0.25 gram 1-phenyl-2-methylurazole (0.0654 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0109	0.0928	0.0843	90.8	9.2
0.0218	0.1114	0.1049	94.0	6.0
0.0328	0.2759	0.2563	92.9	7.1
0.0437	0.2735	0.2535	92.7	7.3

Experiment 3.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0851	0.0764	90.0	10.0
0.0174	0.1850	0.1691	91.3	8.7
0.0261	0.1953	0.1757	89.6	10.4
0.0348	0.2150	0.1958	91.1	8.9

[1] Ber. d. chem. Ges., **41**, 3223.

Experiment 4.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0889	0.0844	94.9	5.1
0.0174	0.1762	0.1632	92.6	7.4
0.0261	0.1976	0.1841	93.1	6.9
0.0348	0.2036	0.1870	92.0	8.0

Experiment 5.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0910	0.0836	91.8	8.2
0.0174	0.1661	0.1494	90.0	10.0
0.0261	0.2105	0.1904	90.5	9.5
0.0348	0.2190	0.1978	90.3	9.7

Experiment 6.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0676	0.0609	90.4	9.6
0.0174	0.1143	0.1031	90.2	9.8
0.0261	0.1538	0.1378	89.6	10.4
0.0348	0.2136	0.1905	89.2	10.8

Experiment 7.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole, and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.1121	0.0989	88.3	11.7
0.0174	0.1822	0.1628	89.3	10.7
0.0261	0.1786	0.1584	88.7	11.3
0.0348	....	....	....	....

Table V.

Per cent. *N*-ester.

Solvent.	0.25 mol. diazo-methane.	0.5 mol. diazo-methane.	0.75 mol. diazo-methane.	1 mol. diazo-methane.
Ether	....	91.7	....	90.6
Chloroform	90.8	(94.0)	92.9	92.7
Acetone	90.0	91.3	89.6	91.0
Ethyl alcohol	(94.9)	92.6	93.1	92.0
Ethyl alcohol and 3 mols. sodium salt	91.8	90.0	90.5	90.3
Methyl alcohol	90.4	90.2	89.6	89.2
Methyl alcohol and 3 mols. sodium salt	88.3	89.3	88.7	....

The 1-phenyl-2,4-dimethylurazole from these experiments melted at 96° and a mixture of this ester and the ester made from sodium 1-phenyl-2-methylurazole and methyl iodide also melted at 96°.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZO-ETHANE.

The experiments with diazoethane were carried out in the same way as those with diazomethane. The diazoethane was made from ethylnitrosourethane as described by von Pechmann.[1]

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.1054	0.0708	67.2	32.8
0.0174	0.1902	0.1302	68.4	31.6
0.0261	0.1048	0.0734	70.0	30.0
0.0348	0.2199	0.1505	68.4	31.6

Experiment 2.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0741	0.0550	(74.2)	(25.8)
0.0174	0.1393	0.0923	(66.2)	(33.8)
0.0261	0.1730	0.1212	70.0	30.0
0.0348	0.1740	0.1227	70.5	29.5

[1] Ber. d. chem. Ges., **31**, 2643.

Experiment 3.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0307	0.0212	69.0	31.0
0.0174	0.0727	0.0488	67.1	32.9
0.0261	0.0763	0.0522	68.4	31.6
0.0348	0.1030	0.0695	67.5	32.5

Experiment 4.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole, and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0862	0.0552	64.0	36.0
0.0174	0.1208	0.0780	64.5	35.5
0.0261	0.1388	0.0864	62.3	37.7
0.0348	0.1707	0.1043	61.1	38.9

Experiment 5.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole and 3 mols. (0.47 gram) sodium iodide, and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0330	0.0227	68.7	31.3
0.0174	0.0409	0.0275	67.2	32.8
0.0261	0.0563	0.0362	66.6	33.4
0.0348	0.0662	0.0452	68.3	31.7

Table VI.

Solvent.	Per cent. N-ester.			
	0.25 mol. diazoethane.	0.5 mol. diazoethane.	0.75 mol. diazoethane.	1 mol. diazoethane.
Acetone	67.2	68.4	70.0	68.4
Ethyl alcohol	....	....	70.0	70.5
Methyl alcohol	69.0	67.1	68.4	67.5
Methyl alcohol and sodium salt	64.0	64.5	62.3	61.1
Methyl alcohol and sodium iodide	68.7	67.2	66.6	68.3

The 1-phenyl-2-methyl-4-ethylurazole melted at 114°.5[1]

[1] THIS JOURNAL, **38**, 76, and page 369 in this article.

and was identical with the ester obtained from sodium 1-phenyl-2-methylurazole and ethyl iodide.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOPROPANE.

Propylurethane was made from ethyl chlorcarbonate and propylamine. A one-liter separating funnel was half filled with water and 9.5 grams ethyl chlorcarbonate dissolved in 100 cc. ether were added. Five grams of propylamine diluted with ether were poured in slowly with frequent shaking and then small amounts of caustic potash solution were added, until the water remained alkaline after vigorous shaking. The ether solution was separated, dried, and evaporated and the propylurethane was distilled. It is a colorless liquid boiling at 191°.5–192°.5 under a pressure of 758 mm. The yield was 7 grams, or 72 per cent. of the theoretical. Analysis:

0.3625 gram substance gave 34.68 cc. nitrogen at 762.25 mm. and 27°.

	Calculated for $C_6H_{13}O_2N$.	Found.
N	10.68	10.56

Propylnitrosourethane was obtained by passing nitrous anhydride into an ethereal solution of propylurethane until it became dark green. The ethereal solution was then washed several times with water, then with sodium carbonate solution, and dried, and the ether was distilled off. The propylnitrosourethane was distilled in a vacuum. It is a reddish oil and resembles methylnitrosourethane in all its properties. From 5.8 grams of propylurethane 4.3 grams, or 70 per cent. of the theoretical yield, of a product boiling at 94° (uncorr.) under a pressure of 35 mm., were obtained. Analysis:

0.1239 gram substance gave 20.5 cc. nitrogen at 768.54 mm. and 27°.

	Calculated for $C_6H_{12}O_3N_2$.	Found.
N	17.50	18.15

The solution of diazopropane was made in the usual way from propylnitrosourethane and alcoholic potassium hy-

droxide. It did not distil over as readily as the diazoethane and the ether solution was a deep yellow-brown. It seemed to react as rapidly as diazomethane and -ethane.

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazopropane solution.

Conc. diazo. sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	....	....	....	....
0.0174	0.1183	0.0819	69.2	30.8
0.0261	0.1733	0.1190	68.7	31.3
0.0348	0.2257	0.1558	69.0	31.0

Experiment 2.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazopropane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.1063	0.0628	59.1	40.9
0.0174	0.1067	0.0635	59.5	40.5
0.0261	0.1148	0.0657	57.2 ⎱	42.8
0.0261	0.1186	0.0715	60.3 ⎰	39.7
0.0348	0.1080	0.0643	58.6 ⎱	41.4
0.0348	0.1370	0.0824	60.1 ⎬	39.9
0.0348	0.1078	0.0629	58.3 ⎰	41.7

Table VII.

Solvent.	Per cent. N-ester.			
	0.25 mol. diazopropane.	0.5 mol. diazopropane.	0.75 mol. diazopropane.	1 mol. diazopropane.
Acetone	....	69.2	68.7	69.0
Methyl alcohol	59.1	59.5	58.8[1]	59.0[2]

The 1-phenyl-2-methyl-4-propylurazole melted at 81°–82° and was in every way identical with the ester obtained from sodium 1-phenyl-2-methylurazole and *n*-propyl iodide.[3] This is especially interesting since we have thus eliminated the

[1] Average of two ratios.
[2] Average of three ratios.
[3] See page 369.

possibility of obtaining an isopropyl ester also. For diazo-propane may have the structure

$$CH_3CH\ CH_2 \text{ or } CH_3CH_2CHN_2.$$
$$\diagdown\diagup$$
$$N_2$$
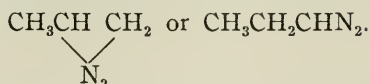
If the first formula were correct we would expect, from the general behavior of such compounds, some isopropyl ester to be formed.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZO-BUTANE.

Butylurethane was made in exactly the same way as propyl-urethane. It is a colorless liquid boiling at 208°–211° (un-corr.) at 770 mm. From 6 grams butylamine 10 grams pure product, or 83 per cent. of the theoretical yield, were obtained.

Butylnitrosourethane was also made in the same way as propylnitrosourethane. It was more viscous than the propyl compound and could not be distilled even in a vacuum; consequently no further attempt was made to purify it. It decomposed violently at its boiling point.

The diazobutane made from the unpurified butylnitroso-urethane was similar to the diazo compounds described before. It evidently is a liquid boiling at a slightly higher temperature than ether, for it did not begin to distil over until most of the ether had already collected in the receiver. The solution was somewhat darker in color than the diazopropane solution. It did not seem to have as disagreeable an odor as diazomethane.

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazobutane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0934	0.0597	63.9	36.1
0.0174	0.2048	. . . .	. . . .	. . . .
0.0261	0.2379	0.1508	63.4	36.6
0.0348	0.2421	0.1537	63.5	36.5
0.0348	0.2326	0.1489	63.9	36.1
0.0348	0.2259	0.1430	63.3	36.6
0.0348	0.2090	0.1319	63.1	36.9

Experiment 2.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazobutane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	0.0352	0.0190	54.0	46.0
0.0174	0.0740	0.0402	54.3	45.7
0.0261	0.0948	0.0510	53.8	46.2
0.0348	0.1587	0.0889	56.0	44.0
0.0348	0.1933	0.1072	55.4	44.5

Table VIII.

	Per cent. N-ester.			
Solvent.	0.25 mol. diazo-butane.	0.5 mol. diazo-butane.	0.75 mol. diazo-butane.	1 mol. diazo-butane.
Acetone	63.9	63.4	63.5	63.4[1]
Methyl alcohol	54.0	54.3	53.8	55.7[2]

The 1-phenyl-2-methyl-4-butylurazole was obtained as an oil which did not crystallize. The compound made from the sodium salt and butyl iodide is also an oil.[3]

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZO-PROPYLENE.

Allylurethane was made in the usual way from allylamine and ethyl chlorcarbonate. From 5 grams of allylamine, 7.5 grams of a colorless oil boiling at 194°.5–195° (uncorr.) under a pressure of 768 mm. were obtained. Yield, 66 per cent. of the theoretical. Analysis:

0.2487 gram substance gave 24.60 cc. nitrogen at 24° and 755.8 mm.

	Calculated for $C_6H_{11}O_2N$.	Found.
N	10.85	11.00

Allylnitrosourethane was made in the same way as the other nitrosourethanes. It is a reddish oil which decomposes when distilled in a vacuum and so no attempt was made to purify it by distillation.

The ether solution of diazopropylene had a deep wine color instead of the usual yellow color of the other diazo solutions.

[1] Average from four experiments.
[2] Average from two experiments.
[3] See page 369.

The diazopropylene acted on the 1-phenyl-2-methylurazole very slowly, several hours being necessary to discharge the color completely. The amount of ester formed in any one case was very small, as the following experiments show:

Experiment 1.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 volume N) and 30 cc. of ethereal diazopropylene.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of N-ester.	Per cent. N-ester.	Per cent. O-ester.
0.0087	. . . .	. . . .	. . . .	. . . .
0.0174	0.0288	0.0194	67.3	32.7
0.0261	0.0368	0.0246	66.8	33.2
0.0348	0.0135	0.0091	67.4	32.6
0.0348	0.0120	0.0079	65.8	34.2

The 1-phenyl-2-methyl-4-allylurazole melts at 61°–64°. The compound was obtained also by the action of allyl iodide on the sodium salt of 1-phenyl-2-methylurazole in alcoholic solution. It melted after crystallization from alcohol at 62°–64° and at 61°–64° when mixed with a sample obtained in the above experiment.

Table IX.—Summary of Experiments in Methyl Alcohol-Ether.

Per cent. N-ester.

Diazoalkyl.	0.25 mol. diazo-alkyl.	0.5 mol. diazo-alkyl.	0.75 mol. diazo-alkyl.	1 mol. diazo-alkyl.
Diazomethane	90.4	90.2	89.6	89.2
Diazoethane	69.0	67.1	68.4	67.5
Diazoethane + sodium salt	64.0	64.5	52.3	61.1
Diazoethane + sodium iodide	68.7	67.2	66.6	68.3
Diazopropane	59.1	59.5	58.8[1]	59.0[1]
Diazobutane	54.0	54.3	53.8	55.7[1]
Diazopropylene	. . . .	67.3	66.8	66.6[1]

Table X.—Summary of Experiments in Acetone-Ether.

Per cent. N-ester.

Diazoalkyl.	0.25 mol. diazo-alkyl.	0.5 mol. diazo-alkyl.	0.75 mol. diazo-alkyl.	1 mol. diazo-alkyl.
Diazomethane	90.0	91.3	89.6	91.1
Diazoethane	67.2	68.4	70.0	68.4
Diazopropane	. . . .	69.2	68.7	69.0
Diazobutane	63.9	. . . .	63.4	63.4[2]

[1] Average from two or more experiments.
[2] Average of two or more ratios.

Table XI.—Summary of Experiments in Ethyl Alcohol-Ether.

Per cent. *N*-ester.

Diazoalkyl.	0.25 mol. diazo- alkyl.	0.5 mol. diazo- alkyl.	0.75 mol. diazo- alkyl.	1 mol. diazo- alkyl.
Diazomethane	94.9	92.6	93.1	92.0
Diazomethane + sodium salt	91.8	90.0	90.5	90.3
Diazoethane	....	....	70.0	70.5

Table XII.—Summary of Experiments in Chloroform-Ether.

Per cent. *N*-ester.

Diazoalkyl.	0.25 mol. diazo- alkyl.	0.5 mol. diazo- alkyl.	0.75 mol. diazo- alkyl.	1 mol. diazo- alkyl.
Diazomethane	90.8	94.0	92.9	92.7

Table XIII.—Summary of Experiments in Ether-Ether.

Per cent. *N*-ester.

Diazoalkyl.	0.25 mol. diazo- alkyl.	0.5 mol. diazo- alkyl.	0.75 mol. diazo- alkyl.	1 mol. diazo- alkyl.
Diazomethane	....	91.7	....	90.6

The above tables show conclusively that constant ratios are obtained for varying amounts of diazoalkyl. The maximum variation in any one series is not over 5 per cent. and the average variation is only about 1.5 per cent., or well within the limit of experimental error. Another fact that is noticed at once is the increase in the amount of oxygen ester with increase in weight of the alkyl group. When we change from diazomethane to diazoethane, in the methyl alcohol solutions, we have a change of 20 per cent. in the ratio of esters, a change of 10 per cent. when we change from diazoethane to diazopropane, and then only a change of 5 per cent. when diazobutane is used. In the experiments in acetone there is about the same difference in the diazomethane and -ethane series. It seems peculiar that here diazoethane and -propane should give about the same ratios. There is, however, a drop of about 5 per cent. in the ratios obtained when diazobutane is used instead of diazopropane. Taken all together, the experiments show conclusively that, as rapid as the alkylations are, K_3 is established so rapidly that it need not be considered to vary with different time periods.

CONCLUSIONS.

1. The conditions affecting the constancy of the ratio of products obtained from a tautomeric substance have been discussed.

2. 1-Phenyl-2-methylurazole has been alkylated with varying molecular proportions of different diazoalkyls and in all cases, for any one series of experiments, a constant ratio of esters has been obtained. This shows conclusively that the constants for the velocity of rearrangement of the two forms of 1-phenyl-2-methylurazole are very large in comparison with K_{trans} and K'_{trans}, or, in other words, K_3 is maintained constant during the alkylation.

3. 1-Phenyl-2-methylurazole and a given diazoalkyl give different ratios of esters in different solvents.

4. 1-Phenyl-2-methylurazole and different diazoalkyls give different ratios of esters in the same solvent.

5. Evidence has been given to show how we may have abnormal hydrolysis of the sodium salt of 1-phenyl-2-methylurazole. In the presence of sodium 1-phenyl-2-methylurazole the 1-phenyl-2-methylurazole gives with diazomethane and with diazoethane ratios of esters which are different from the ratios obtained when no sodium salt is present. This leads us to the conclusion that the equilibrium point of the two (or more) tautomeric forms of the sodium salt may be different from that of the two tautomeric forms of the acid, and hence gives a possible explanation of abnormal hydrolysis. These conclusions have been further strengthened by the work of Mr. E. K. Marshall, who has attacked this problem by more direct methods.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, JUNE 1, 1909.

OBITUARIES.

FRIEDRICH KOHLRAUSCH.

Friedrich Kohlrausch, who died suddenly on January 17th, was born at Rinteln on October 14, 1840. He received his early schooling at Rinteln, Kessel–Marburg and Erlangen, and then studied at Göttingen and Erlangen, obtaining his

doctor's degree at the latter university in 1863. He was assistant for a short time at the Göttingen observatory and from 1864 to 1866 was privatdozent of the Physikalischer Verein at Frankfort. Weber having offered him an assistantship, he returned to Göttingen and in the following year was made Professor Extraordinarius. During the four years he remained here, he was not only actively engaged in research work, but succeeded in establishing experimental physics as a branch of the University instruction. It was during this period that his great work on the conductivity of electrolytes was begun; the first record of the use of the alternating current in the study of this problem is dated May 19, 1868. In 1870 he accepted a call to the Zürich Polytechnic Institute, but the following year he went to Darmstadt. In 1875 he succeeded Kundt at Würzburg and again in 1888 at Strassburg when Kundt was called to Berlin. In 1895, on the death of Helmholtz, Kohlrausch was elected president of the Physikalisch-technische Reichsanstalt, and remained at its head till 1905, when ill health compelled him to retire. In 1900 he had been made honorary professor in the University of Berlin and in 1908 the Deutsche Bunsen-Gesellschaft awarded him its first Bunsen medal. The last five years of his life were spent in the quietude of his home at Marburg and at Jugenheim, but he continued his investigations with unabated vigor to the very last.

His greatest work is, of course, the investigation on the conductivity of electrolytes, which proved so fruitful in his hands. We need only mention the discovery of the law of the independent migration of ions, the bridge and telephone method of measuring conductivities, the determination of the conductivity and dissociation constant of pure water, the method for the determination of the solubility of difficultly soluble substances from their conductivity, etc. Of less interest to chemists, but marked by no less skill, resourcefulness and deep insight are his investigations on terrestrial magnetism, elasticity, heat and electrical conduction. As a teacher, his influence has become widely felt, and his book, "Leitfaden der praktischen Physik," the eleventh edition of which was published just before his death, is probably used, at one time or other, by every student of physics in Germany and by many outside of Germany.

WILLARD BRADLEY RISING.

The death of Professor Willard Bradley Rising was announced February 9th. Prof. Rising was born at Mechlenburg, N. Y., on September 26, 1839. He attended Hamilton

College, New York, from which he graduated in 1864. After receiving the degree of M.E. from the University of Michigan in 1867 he taught two years at the then College of California and then went to Germany, where he obtained his doctorate from Heidelberg in 1871. He studied under Hofmann at Berlin for a time and in 1872 was appointed to the chair of chemistry at the University of California, a position which he held without interruption till his death. Since 1885 he had been state analyst of California and for several years was consulting analyst of the State Board of Viticulture, carrying out investigations on the chemistry of wine. In his capacity as consulting analyst of a large powder company he has contributed also to the chemistry of explosives.

REVIEWS.

OUTLINES OF CHEMISTRY. By LOUIS KAHLENBERG, PH.D., Professor of Chemistry and Director of the Course in Chemistry in the University of Wisconsin. New York: The Macmillan Company. 1909. pp. xix + 548. Price, $2.60.

The fact that he has more than six hundred students under his instruction amply justifies the author in preparing a new text-book for college students. In his position it is desirable that he should satisfy his own views of what should be taught, and how it should be done.

The book is without doubt a very creditable piece of work. The facts and theories are, in general, well selected and presented. An important feature is the emphasis put upon technical applications and processes, which include some of the most recent developments in applied chemistry. It may be observed that the descriptive matter appears to be rather more extensive than is usual in books of this class, while the theory is perhaps somewhat less fully treated than is commonly the case. As a whole, the book may be regarded as presenting a course sufficiently extensive for the average college student.

It is not to be expected that any book will be perfect, but attention may be called to some metallurgical weaknesses which this book exhibits, as is the case with practically all of our text-books on general chemistry. For instance, the use of superheated steam in the Parke's process is here described as applied to the wrong material. The relationship between cast iron and steel is described in a way that is misleading, for it would be inferred that graphite crystallizes out from steel on annealing, while the hardening of steel by

quenching and the chilling of gray cast iron in casting appear to be viewed as identical processes. The characterization of gray and white cast iron as being produced, respectively, by the very slow and the rapid cooling of "cast iron" is entirely wrong, except as far as it applies to the "chilling" of gray iron.

The feature of this book which is likely to attract the most attention is the author's well-known attitude in rejecting as untenable the ionic theory of Arrhenius, and his antagonism towards van't Hoff's application of the laws of gases to solutions. In this attitude he stands practically alone among the present generation of chemists. This feature, however, may be considered as of minor importance, for it must be admitted that he gives a fair discussion of the views which he rejects, and it is quite possible that some moderate adherents of the ionic theory will prefer this treatment of it to its too enthusiastic employment.   HORACE L. WELLS.

HEAT ENERGY AND FUELS, PYROMETRY, COMBUSTION ANALYSIS OF FUELS AND MANUFACTURE OF CHARCOAL, COKE AND FUEL GAS. By HANS V. JÜPTNER, Professor Imperial Royal and Technical Institute, Vienna. Translated by OSKAR NAGEL, PH.D. New York: McGraw Publishing Co. 1908. pp. v + 305. Price, $3.

The author treats the subject of chemical technology in four volumes and divides it into (1) chemical technology of energy; (2) chemical technology of materials. The present volume is the first one of the series and deals with the first subject. The English translation of this book is a welcome addition as it brings to our attention a valuable work on the subject of fuels. It contains three hundred pages and, exclusive of the introduction, is divided into twenty-three chapters, as follows: Measurement of High Temperatures, Pyrometry (continued), Pyrometry (conclusion), Combustion Heat and Its Determination, Direct Methods for Determining the Combustion Heat, Incomplete Combustion, Combustion Temperature, Fuels (in general), Wood, Fossil Solid Fuels (in general), Peat, Brown Coal, Bituminous and Anthracite Coals, Artificial Solid Fuels, Charcoal, Peat Coal, Coke and Briquettes, Coking Apparatus, Liquid Fuels, Gaseous Fuels, Producer Gas, Water Gas, Dowson Gas, Blast Furnace Gas and Regenerated Combustion Gases, Apparatus for the Production of Fuel Gases.

This book is intended for use in universities and engineering schools as well as for practicing engineers, as the subject is treated both theoretically and practically. It is made specially valuable because of the large amount of tabulated

data on most of the subjects discussed.   Much of this material
is not readily accessible and is presented here in convenient
form and for this reason the book will commend itself to the
practising engineer.

The chapters on pyrometry and heat of combustion are
very comprehensive and it may be questioned whether in
these chapters certain inaccurate methods might not have
been treated more briefly to advantage.

The reviewer would like to call attention to the table on
page 243, giving the composition of Pennsylvania natural
gas as follows:

Methane	67 per cent.	Ethylene	1 per cent.
Hydrogen	22 per cent.	Carbon dioxide	0.6 per cent.
Nitrogen	3 per cent.	Carbon monoxide	0.6 per cent.
Ethane	5 per cent.		

The most accurate analyses of natural gas around Pitts-
burg show it to be composed almost entirely of the lower
paraffins· and nitrogen.   It contains no free hydrogen or
carbon monoxide and only traces of carbon dioxide.   The
book will undoubtedly be of great use to students and espe-
cially useful to the practical worker.   J. C. W. FRAZER.

THE CHEMICAL ANALYSIS OF IRON.   A Complete Account of All the Best
    Known Methods for the Analysis of Iron, Steel, Pig Iron, Iron Ore,
    Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer
    Gases. BY ANDREW ALEXANDER BLAIR. Seventh Edition. Phila-
    delphia and London: J. B. Lippincott Co. 1908. pp. xix + 334.
    Price, $4.

That this book is in demand and authoritative is shown by
the rapidity with which it has passed through its various
editions.   This edition contains as new matter a method
for the separation of vanadium, molybdenum, chromium,
and nickel in steel, the volumetric cyanide process for nickel,
and some improvements in the methods for gas analysis.
In all other respects it remains the same and the best of its
class.

To the reviewer, who has used the book since the second
edition appeared, it has always been a matter of surprise
that the author has not made more of an attempt to make
the book one which could be used as a text for students.   In
very few cases does the author illustrate clearly or at all the
principles involved in the methods.   It is essentially a state-
ment of details, and frequently the student, and in some cases
the average chemist, is lost in a maze of detailed facts.   The
reviewer has particularly in mind the acetate method for
phosphorus.   The lack of principle is again shown on page

100 where the author gives an example of the conversion of a potassium permanganate solution, standardized against iron, into its value in terms of phosphorus. To a teacher trying to instil principles this is hopeless, and to any one knowing anything of the significance of figures or precision of measurements, ludicrous. Other cases might be cited.

In a new edition the book could be pruned advantageously. It contains some antiquated methods, such as some of the methods for carbon, which are of importance only from the historical point of view.   H. F.

METALLOGRAPHIE. Ein ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen and technischen Eigenschaften der Metalle und metallischen Legierungen. Von DR. W. GUERTLER, Privatdozent an der Königl. Technischen Hochschule zu Berlin. Erster Band : Die Konstitution. Heft I. Berlin: Gebrüder Bornträger. pp. 80. 1909. Price, M. 4. 20.

PHYSIKALISCHE CHEMIE DER METALLE. Sechs Vorträge über die wissenschaftlichen Grundlägen der Metallurgie. Von DR. RUDOLPH SCHENCK, Professor der physikalischen Chemie an der Königl. Technischen Hochschule zu Aachen. Halle : Wilhelm Knapp. 1909. pp. 187. Price, M. 7.00.

LEÇONS SUR LES ALLIAGES MÉTALLIQUES. PAR J. CAVALIER, Professeur Honoraire à la Faculté des Sciènces de l'Université de Rennes. Paris : Vuibert et Nony. 1909. pp. xix + 466.

METALLOGRAFIA, APPLICATA AI PRODUTTI SIDERURGICI. UMBERTO SAVOIA. Assistente di Metallurgia nel R. Instituto Tecnico Superiare di Milano. Milano : Ulrico Hoepli. 1909. pp. xvi + 205. Price, £3.50.

The rapidly growing importance of the subject of Metallography is shown in the recent publication of many books upon various phases of the subject. The accumulation of data has recently been very rapid, and much of this material is now being collected in book form. The subject has been slow in developing when we consider that the scientific foundations were laid by Sarby as early as 1864. Previous to this time there was a vast number of isolated facts, but the methods which were employed in the study of metals and alloys were so crude that rapid development could not have been expected. With the introduction of physico-chemical methods in the study of binary mixtures, and the application of the phase rule, this hitherto chaotic field has been extensively worked, and a new science has been established. By means of the thermocouple and the microscope a science has been founded in which accurate facts replace mere suppositions, and by which such complicated alloys as steel, the brasses and bronzes may be satisfactorily explained.

Dr. Guertler has planned a comprehensive treatise on

Metallography, and proposes to treat of the physical, chemical and technical sides of the subject. In this volume, which deals almost exclusively with the theoretical part of the subject, he discusses the constitution of binary alloys. He reviews the early development of the science, considers the thermal equilibrium diagrams from the point of view of the phase rule, and discusses in detail the subject of solid solutions and compounds. As types of solid solutions, the author gives a detailed discussion of the cooling curves of the manganese-iron, iron-cobalt, and nickel-cobalt alloys, and these will probably be followed by similar examples in the next volumes.

The book is distinctly of an advanced type and will be difficult reading to all except those having had some training in physical chemistry. It will, however, be a very valuable addition to the subject of Metallography, and it is sure to be authoritative. The printing is excellent and the marginal notes very useful. It is sincerely hoped that the succeeding volumes will follow quickly.

Of an entirely different character is the book by Dr. R. Schenck, in which he also treats of the constitution of alloys, but he uses this as a means of preparing his reader for broader problems in equilibrium phenomena. The book consists primarily of a course of six lectures serving as a physico-chemical introduction to the study of metallurgy. The author discusses the physical changes of the metals, the theories of metallic solutions, and the thermal equilibrium diagrams of binary and ternary metallic mixtures. In the application of the theories, the author discusses briefly some binary alloys, and more fully the iron-carbon alloys, and alloys of metals with the nonmetals, such as Cu-Cu_2O, Cu-Cu_2S, Fe-FeS, Pb-PbS, Ni-NiS, Fe-Fe_3P, and some double sulphides. Three chapters are devoted especially to metallurgical reactions such as oxidation and reduction and the equilibrium between various metals and oxygen, or sulphur. Especially important to those interested in the metallurgy of iron is the application of the phase rule in explaining the equilibrium in the system iron, carbon, oxygen. Similar application is made to nonferrous metallurgy.

The book is an excellent treatise on the principles upon which the science of metallurgy is founded. It is concise, clear, well illustrated with diagrams, tables, and photomicrographs.

The book by Professor Cavalier is an exhaustive treatise on the physical and chemical properties of metals and their

alloys, and to any one interested in the properties of metals it will furnish an excellent guide to the theoretical and practical sides of the subject. The author describes the physical properties of the industrially important metals, such as strengh, malleability, hardness, electrical conductivity, magnetism, thermo-electric properties, etc., and the methods for determining these values. The various forms of furnaces, including the recently developed electrical furnaces, are discussed with sufficient detail to give a fair idea of their use. The subject of pyrometry is adequately dealt with, and the author describes some of the various forms of apparatus for measuring high temperatures. The technique of mechanical testing and microscopic metallography is given.

In regard to the more theoretical side of the subject, the author discusses the commercially important binary alloys from the point of view of the phase rule, and with the brasses, bronzes, and bearing metals much technical information is also given. Almost 100 pages of the book are devoted to the consideration of iron and its alloys with carbon, manganese, nickel, chromium, etc., and to the special alloy steels. This part of the book is replete with the most recent information and is an excellent compilation of much widely scattered material.

As a whole, the book deserves much praise, and should be of value to the metallurgist and testing engineer. Many references are given throughout the text, but the book would be of much greater value if the references were more complete.

The book by Savoia is a concise and practical discussion of the principle and technique of the metallography of steel and iron. It discusses briefly the history of the science, the preparation, polishing and etching of specimens; and more fully the structural constituents of iron, iron-carbon alloys, nickel and chrome-nickel alloy, and the various classes of cast irons. The book is excellently illustrated with a large number of photomicrographs, of which there is some unnecessary duplication. The book should be of considerable value to the Italian engineer and metallurgist.   H. F.

ANLEITUNG ZUM EXPERIMENTIEREN IN DER VORLESUNG ÜBER ORGAN-
    ISCHE CHEMIE. Von DR. HANS RUPE, A. O. Professor an der Uni-
    versität Basel. Mit 30 in den Text eingedruckten Abbildungen.
    Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn.
    1909. S. x + 130. Preis: geheftet, M. 4.50; geb., M. 5.40.

This excellent book is presented to organic chemists as a guide for lecture experiments, of which certainly too few are given in America, even to beginners, in the organic field. The

freshman is dazzled with the illumination of the metals and non-metals through lecture-table pyrotechnics, but when he comes later to the far more abstruse problems of carbon chemistry, he is left in the utter darkness of his own efforts at enlightenment. The beginner in organic chemistry needs instructive and impressive lecture-table experiments *and* the usual laboratory course just as much as he did in the inorganic work.

The author acknowledges that, on account of his love for the beauty of the experiments in the aliphatic series, he has through neglect treated the benzene series very much like a mother-in-law. Nevertheless, besides the large number of instructive experiments with aliphatic compounds, he gives a good list of preparations of aromatic compounds. After all, chemists see no very sharp dividing line between the properties of the aliphatic and the aromatic compounds.

The most striking experiments in the benzene series are those involving the dyes, and Professor Rupe has treated the preparation and properties of phenolphthalein, fluorescein, eosin, Congo red, fuchsine, alizarin and indigo very fully.

S. F. ACREE.

AMERICAN

CHEMICAL JOURNAL

THE REPLACEMENT OF HALOGEN BY THE NITRO GROUP.

[FIRST PAPER.]

By L. Chas. Raiford and Fred. W. Heyl.

It has long been known[1] that 2,4,6-tribromphenol can be made to interact with nitric acid in such a way that the halogen atom para to the hydroxyl group is replaced by a nitro group. Later it was found by Claus and Hirsch[2] that 2,4,6-tribrom-*m*-cresol gives similar results, and they reported the isolation of the para compound, 2,6-dibrom-4-nitro-*m*-cresol, as the product. But in no case, so far as we are aware, has more than one nitro compound been obtained at once as the result of the action specified.

In 1900 Zincke[3] undertook the nitration of 2,4,6-tribrom-*m*-cresol by treatment of a glacial acetic acid solution of the substance with solid sodium nitrite. From the reaction mixture thus obtained he reported the isolation of but a single substance, a mononitrodibrom-*m*-cresol in which the halogen

[1] Armstrong and Harrow: Jahres. d. Chem., **1876**, 448.
[2] J. prakt. Chem., [2] **39**, 61 (1889).
[3] *Ibid.*, [2] **61**, 564 (1900).

atom para to the hydroxyl group had been replaced by the
nitro group. In an attempt to prepare stereoisomeric chlor-
imidoquinones, one[1] of us, working with Stieglitz, had occasion
to repeat Zincke's work with tribrom-*m*-cresol, and found that
when the reaction is allowed to proceed at a temperature of
12°–15° (Zincke gave no statement relative to the tempera-
ture at which he carried on his experiments) it gives a mix-
ture of two isomeric mononitrodibrom-*m*-cresols, in which
the nitro groups introduced are ortho and para, respectively,
to the hydroxyl group. The ease with which this reaction
took place, and the excellent yields of the isomers obtained,
suggested the possibility of replacing halogen by the nitro
group under similar conditions in other compounds. It was
therefore decided to study the reaction more carefully, first
with a well-known bromine derivative. Accordingly, 2,4,6-
tribromphenol was selected for the starting material.

· EXPERIMENTAL PART.

Nitration of Tribromphenol.—2,4,6-Tribromphenol,[2] pre-
pared in the usual manner, carefully freed from tribrom-
phenolbrom, and repeatedly crystallized from dilute alcohol
until it melted constantly at 93° (uncorrected), was dissolved
in about twelve times its weight of glacial acetic acid, and the
resulting solution cooled to 12°–15°. To this was gradually
added ten per cent. more than the calculated amount of solid
sodium nitrite, during which time the flask was continually
shaken and the temperature kept down to that specified
above. When all the nitrite had dissolved the dark-colored
liquid was poured, with stirring, into five volumes of cold
water, and the mixture allowed to stand for some hours. At
the end of this time the yellow solid was collected on a filter,
washed with water, and dried on a porous plate. The weight
of the mass at this point represented 97 per cent. of the
theoretical yield, calculated on the basis of the formation of
mononitro compounds alone.[3] The crude product began to

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[1] Results soon to be published from the Kent Chemical Laboratory of the Uni-
versity of Chicago.

[2] Laurent: Ann. Chem. (Liebig), **43**, 212.

[3] As will be shown later, a portion of this was unchanged tribromphenol.

melt at 74° and was completely liquid at 94°—behavior that indicated the possible presence of more than one compound. It may be stated at once that two isomeric mononitrodibromphenols were isolated from the mixture,
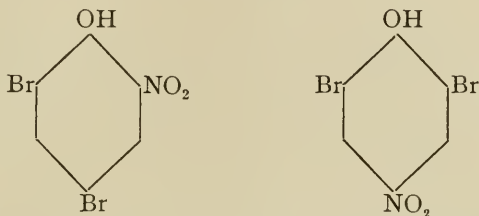
4,6-dibrom-2-nitrophenol, melting at 117°, and 2,6-dibrom-4-nitrophenol, melting at 141°.

Separation of the Isomers.

The Para Compound.—Consideration of the properties of the two dibromnitrophenols recorded by Beilstein led, at first, to the attempt to separate them by distillation with steam, but this was found to be unsatisfactory. Separation by fractional crystallization of their potassium salts was found to be possible, though it involved much time. The best method of separation depends on the difference in solubility of the isomers in a mixture of chloroform and ligroin. A portion of the dried crude product, secured as indicated above, was dissolved in warm chloroform (1 gram to 0.75 cc.) and to the clear solution was added two volumes of ligroin, boiling at 40°–60°. Precipitation of nearly all the high-melting isomer (para compound) took place at once. After standing half an hour the solid was removed by filtration and crystallized twice from benzene, when nearly colorless crystals, melting at 141° and decomposing when heated above this point, were secured. In order to show that the compound here isolated is identical with 2,6-dibrom-4-nitrophenol, a small quantity of the latter was prepared by brominating 4-nitrophenol.[1] A mixture of the two products melts at the same temperature as either of them separately. The product ob-

[1] Brunck: Z. Chem., **1867**, 204.

tained by nitrating tribromphenol was analyzed for bromine.
0.1563 gram substance gave 0.1976 gram AgBr.

	Calculated for $C_6H_3O_3NBr_2$.	Found.
Br	53.87	53.82

The Ortho Compound.—When the filtrate obtained by removal of the para compound was allowed to evaporate to dryness it left a yellow solid melting at 80°–90°. This was crystallized several times from 95 per cent. alcohol until crystals melting constantly at 117° were secured. Some of this product was mixed with 4,6-dibrom-2-nitrophenol prepared according to Goldstein's[1] directions, and the mixture melted at 117°, showing the products to be identical. Analysis of the product obtained from tribromphenol gave the following result:

0.1329 gram substance gave 0.1689 gram AgBr.

	Calculated for $C_6H_3O_3NBr_2$.	Found.
Br	53.87	54.08

The mother liquor left after removal of the ortho compound was evaporated to dryness and gave a yellow solid that melted at 70°–77°, and which was thought, at first, to consist of traces of the ortho body, with possibly a third nitro compound. The material was purified by conversion into the barium salt in the usual way, and the latter was obtained in the form of yellow needles arranged in fan-shaped clusters, containing one molecule of water of hydration. A portion of this salt was dissolved in water and decomposed by dilute hydrochloric acid, when a colorless substance was secured. This was crystallized from dilute alcohol, out of which it separated in the form of long silky needles melting at 93°. A mixture of this substance with the tribromphenol used as starting compound still melted at 93°. Analysis of the recovered material for bromine resulted as follows:

[1] J. russ. chem. Ges., **10**, 354.

0.2028 gram substance gave 0.3446 gram AgBr.

	Calculated for C$_6$H$_3$OBr$_3$.	Found.
Br	72.50	72.37

A second portion of the barium salt mentioned above was heated to constant weight at 110°–115°, and the residue was then analyzed for barium:

0.1820 gram crystals lost, on drying, 0.0042 gram H$_2$O.

0.1820 gram crystals gave 0.0520 gram BaSO$_4$.

	Calculated for (C$_6$H$_2$OBr$_3$)$_2$Ba.H$_2$O.	Found.
H$_2$O	2.20	2.30
Ba	16.84	16.81

The Behavior of Trichlorphenol.—In an attempt to prepare the dihalogenated nitro-*m*-cresols, Raiford[1] found that while the dibromnitro-*m*-cresols could easily be obtained by treatment of 2,4,6-tribrom-*m*-cresol in glacial acetic acid solution with sodium nitrite, 2,4,6-trichlor-*m*-cresol could not be made to undergo the reaction. It became a matter of interest, therefore, in the present investigation, to examine 2,4,6-trichlorphenol in this direction. A portion of the compound was prepared by a modification of Chandelon's[2] method, which involved a much simpler, cleaner and more rapid method of securing the necessary hypochlorite solution. The latter was obtained according to Graebe's[3] method, and was then used as specified by Chandelon. The trichlorphenol obtained was carefully purified by dissolving it in a solution of sodium hydroxide, and treating this solution with carbon dioxide, which precipitated pure trichlorphenol, melting at 68°. When this was dissolved in glacial acetic acid, and sodium nitrite was mixed with the solution, as detailed above, the solid that separated when this solution was poured into water melted at 68°, and was, in fact, unchanged 2,4,6-trichlorphenol, which shows that the chlor compound is far less re-

[1] Unpublished reports.
[2] Bull. Soc. Chim., **38**, 116 (1882).
[3] Ber. d. chem. Ges., **35**, 43 and 2753 (1902).

active, under the conditions of this experiment, than the corresponding brom compound. Analysis of the recovered material for halogen gave the following result:

0.1040 gram substance gave 0.2254 gram AgCl.

	Calculated for $C_6H_3OCl_3$.	Found.
Cl	53.89	53.61

The work will be continued in this laboratory.

LARAMIE, WYOMING,
January, 1910.

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CLXXX.—ON ALKYLATION OF AROMATIC AMINO ACIDS:
5-IOD-2-AMINOBENZOIC ACID AND 3,5-DIIOD-2-AMINO-BENZOIC ACID.

[SECOND PAPER.]

BY HENRY L. WHEELER AND CARL O. JOHNS.

When the salts of *o*-, *m*- and *p*-aminobenzoic acids are treated with alkyl halides, nitrogen alkyl derivatives result. From the work which has been published on this subject it appears that the action first takes place by addition, and then substitution, in the amino group, and no direct replacement of the metal by the alkyl group occurs. After substitution of hydrogen in the amino group, the alkyl group may then attach itself to oxygen and form an ester, either by directly replacing the metal of the carboxyl or by a rearrangement of a betaine.

Griess[1] found that the potassium salt of *m*-aminobenzoic acid and ethyl iodide, in whatever proportion they were mixed, gave a mixture of mono- and diethylaminobenzoic acids.

The above potassium salt and allyl iodide invariably gave only a diallylaminobenzoic acid and no trace of a mono derivative. On the other hand, the potassium salt of aminoanisic

[1] Ber. d. chem. Ges., **5**, 1038 (1872).

acid and methyl iodide gave a monomethylaminoanisic acid.

In his next article Griess[1] showed that *m*-aminobenzoic acid gives, with three molecular proportions of potassium hydroxide and three of methyl iodide, the hydriodide of the deliquescent benzbetaine, trimethylaminobenzoic acid, when the residue, after evaporation, is treated with hydriodic acid. The betaine is a crystalline solid which loses one molecule of water at 105° and which, on heating, rearranges into methyldimethylaminobenzoate (oil):

$$C_6H_4 \underset{CO-\text{——}}{\overset{N(CH_3)_3}{<\quad>}} O \longrightarrow C_6H_4 \underset{COOCH_3}{\overset{N(CH_3)_2}{<}}.$$
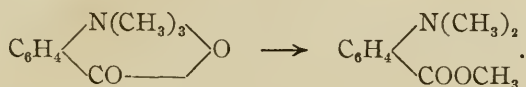
Trimethylanisbetaine was prepared and found to behave in a similar manner.

Michler[2] heated *p*-aminobenzoic acid with three molecular proportions of potassium hydroxide and two of methyl iodide and obtained *p*-dimethylaminobenzoic acid. The diethylamino acid was then prepared in a similar manner.[3]

Michael and Wing, in a paper on the action of alkyl iodides on amino acids, state that in the case of *p*-aminobenzoic acid three molecular proportions of methyl iodide and an excess of potassium hydroxide give the mono- and dimethylamino acids and also the betaine. With ethyl iodide no betaine was obtained, the product being the ethyl ester of the diethylamino acid, $(C_2H_5)_2NC_6H_4COOC_2H_5$, and with three proportions of allyl iodide and an excess of alkali the sole product was diallylaminobenzoic acid. They state that they were unable to find that either the betaine or the allyl ester of the acid were ormed.

In 1893 Lauth[4] examined the behavior of *o*-aminobenzoic acid, neutralized with sodium hydroxide, towards two molecular proportions of methyl iodide in alcoholic solution, and obtained the dimethylaminobenzoic acid. The dimethyl-

[1] Ber. d. chem. Ges., **6**, 586 (1873).
[2] *Ibid.*, **9**, 401 (1876).
[3] *Ibid.*, **9**, 1912 (1876).
[4] Bull. Soc. Chim., [3] **9**, 970 (1893).

amino derivatives of the *meta* and *para* acid were likewise prepared. From the *ortho* acid he also obtained the quaternary derivatives, $NaO.COC_6H_4N(CH_3)_3I$, $HOCOC_6H_4N(CH_3)_3I$, and $HOCOC_6H_4(CH_3)_3OH$. The first of these quaternary derivatives was best obtained by allowing three molecular proportions of methyl iodide to act on the sodium salt of anthranilic acid. The formation of this compound goes to show that the first product of the reaction is not an ester. The monomethylanthranilic acid was prepared in a similar manner by Fortmann.[1]

H. Meyer[2] found, in 1900, that by the action of alkyl iodides on the potassium salt of *o*-aminobenzoic acid dissolved in 10 parts of water an excellent yield of the monoalkylamino derivatives was obtained. He prepared in this manner monomethyl-, ethyl-, normal propyl-, isobutyl- and isoamylanthranilic acids. Chloracetic acid[3] and ethylene bromide[4] also give *N*-derivatives.

The point to be emphasized in the above researches is that no one has observed the formation of esters of the type

$$H_2NC_6H_4COOR$$

by the action of alkyl halides on the alkali salts of the simple aminobenzoic acids.

On the other hand, by the above method, certain substituted aminobenzoic acids give esters of this type in which the hydrogen of the amino group is not substituted and from which the unaltered acid can be obtained by saponification.

The writers' attention was called to this fact when in a recent investigation it became desirable to characterize 3,5-diiod-4-aminobenzoic acid[5] by a derivative having a melting point. It was then found that the potassium salt of this acid and ethyl iodide gave an ester and not an alkylamino acid.

A search in the literature has revealed the fact that not only

[1] J. prakt. Chem., [2] **55**, 123 (1897).
[2] Monats. Chem., **21**, 932.
[3] Mauthner and Suida: Monats. Chem., **9**, 728 (1888); **11**, 380 (1890).
[4] Schiff and Parenti: Ann. Chem. (Liebig), **226**, 244 (1884).
[5] This JOURNAL, **42**, 455 (1909).

the silver salt of 3,5-dinitro-4-aminobenzoic acid[1] but also 3-nitro-2-aminobenzoic acid, either in the form of the silver salt at 20°–100°[2] or the potassium salt at 130°–140°,[3] gave an ester.

The result in the case of the mononitroamino acid is noteworthy since two other isomeric mononitroamino acids have been examined and have been found to alkylate on the amino group.

Rollwage[4] states that 3-nitro-5-aminobenzoic acid gives a *N*-ethyl acid, while Wheeler and Barnes[5] obtained from the silver salt of 4-nitro-2-aminobenzoic acid the *N*-compounds

$$C_2H_5NHC_6H_3.NO_2COOH$$

and, in smaller amount,

$$C_2H_5NHC_6H_3NO_2COOC_2H_5.$$

It will be noticed in all the above cases that when the amino group is surrounded by two substituents or radicals, I and I, COOH and NO_2, or NO_2 and NO_2, alkylation takes place on the oxygen and not on the nitrogen.

In accordance with this, we now show that 5-iod-2-aminobenzoic acid gives a *N*-alkyl derivative, while 3,5-diiod-2-aminobenzoic acid gives an ester. In the latter case the adjacent groups are COOH and I.

Whether this difference in behavior is due to stereochemical interference or to both this influence and that of negative groups—the above substituents have a negative character—must be left to be investigated, and we wish to reserve the work for this laboratory.

It would be expected that substituted aromatic amino acids would share, at least to some extent, the properties of the corresponding substituted aromatic amines. Stereochemical interference or retardation (*sterische Verlangsamung*[6])

[1] Salkowski: Ann. Chem. (Liebig), **163**, 11 (1872).
[2] Hübner: *Ibid.*, **195**, 40 (1879).
[3] Zacharias: J. prakt. Chem., **43**, 437 (1891).
[4] Ber. d. chem. Ges., **10**, 1704 (1877).
[5] THIS JOURNAL, **20**, 217 (1898).
[6] Bischoff: Jahrbuch d. Chem., **1903**, 172

has frequently been noted in the various stages of alkylation in these cases. It has been observed among aromatic amines that groups in both of the *ortho* positions (alkyl, phenyl, bromine, nitro and acetamino) completely[1] prevent the formation of quaternary bases and that a single *ortho* substituent reduces the rate or tendency of the amine to alkylate;[2] while 1-methyl-2-amino-3-isobutylbenzene, at 150°, is attacked to only a slight extent[3] and diaminomesitylene is not altered at all by alkyl halides.[4] Methyl sulphate has been found to alkylate where alkyl halides fail.

On the other hand, groups in the *ortho* positions to the carboxyl fail to prevent the alkylation of this group by alkyl halides[5] and it also appears that groups situated in the same manner in reference to a hydroxyl do not protect this group from alkylation, as, for example, in 3,5-diiod-4-hydroxybenzoic acid[6] and 3,5-diiodtyrosine.[7]

The results obtained in the alkylation of substituted amino acids not only have theoretical significance but they also may prove to be of practical value in separating mixtures of acids and isolating the adjacent derivatives. Some of these acids, which are frequently formed among isomers in smallest amount, have been obtained from mixtures only by tedious crystallizations of their salts.

We have also found that 3,5-diiod-2-aminobenzoic acid gives an acid chloride when it is suspended in benzene and phosphorus pentachloride is added. The product with alcohol gives the same ester as is obtained by alkylating the potassium salt with ethyl iodide.

When the acid chloride is treated with potassium sulphydrate it yields the potassium salt of 3,5-diiod-2-aminothiolbenzoic

[1] Hofmann: Ber. d. chem. Ges., **5**, 718 (1872). Fischer and Windaus: *Ibid.*, **33**, 345, 1967 (1900). Pinnow: *Ibid.*, **32**, 1401 (1899); **34**, 1129 (1901).

[2] Fries: Ann. Chem. (Liebig), **346**, 190 (1906).

[3] Effront: Ber. d. chem. Ges., **17**, 2317 (1884).

[4] Morgan: P. Chem. Soc., **18**, 87 (1902). Schmidt: Ueber den Einfluss der Kernsubstitution auf die Reaktionsfähigkeit aromatischer Verbindungen; Chem. u. chem.-tech. Vorträge, **8**, 314 (1902).

[5] Sudborough: J. Chem. Soc., **67**, 587 (1895).

[6] THIS JOURNAL, **42**, 460 (1909).

[7] *Ibid.*

acid, from which we have prepared and examined the thiol acid and its disulphide. This is probably the first representative of a thiol acid containing a free amino group.

EXPERIMENTAL PART.
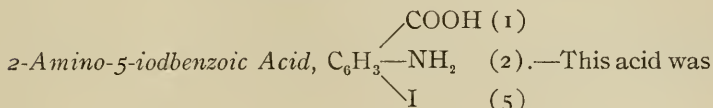
2-Amino-5-iodbenzoic Acid, C_6H_3
$\begin{array}{l} \diagup COOH\ (1) \\ -NH_2 \quad (2) \\ \diagdown I \qquad (5) \end{array}$
.—This acid was first obtained by Grothe.[1] Its structure was determined by Wheeler and Liddle[2] by oxidizing 1-methyl-2-acetylamino-5-iodbenzene with potassium permanganate. It is far more easily obtained by directly iodating anthranilic acid.

Five grams of anthranilic acid were dissolved in 50 cc. of water containing 2.1 grams of potassium hydroxide. Nine and two-tenths grams of powdered iodine were added in small portions and the mixture was frequently shaken. The iodine was rapidly absorbed, causing the formation of a brown precipitate. This crude product weighed 9.0 grams, or 93 per cent. of the calculated. When crystallized from alcohol it formed colorless prisms that decomposed at 210°. When mixed with a sample of 2-amino-5-iodbenzoic acid from our previous work, the mixture also melted at 210°.

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.32	5.55

Action of Ethyl Iodide on the Potassium Salt.—One gram of potassium hydroxide was dissolved in 40 cc. of water and 4.7 grams of pulverized 2-amino-5-iodbenzoic acid were added to the solution. A slight trace of acid remained undissolved and was filtered off. The solution was mixed with 60 cc. of alcohol and 15 grams of ethyl iodide and this mixture was heated for 3 hours on a water bath. When the solution was evaporated to dryness it left a residue which dissolved completely in ammonia and was reprecipitated by acetic acid in small clusters of minute prisms. The yield was 71 per cent.

[1] J. prakt. Chem., [2] **18**, 326 (1878).
[2] THIS JOURNAL, **42**, 499 (1909).

The product melted to a black oil with effervescence at 162°
and the melting point was not raised by recrystallizing twice
from alcohol. It is easily soluble in ether, hot benzene and
alcohol, and insoluble in water. Its solubility in dilute am-
monia and the following analysis showed that it was not an
ester. The acid had therefore alkylated on the nitrogen,
forming *2-ethylamino-5-iodbenzoic acid.*

0.1790 gram substance gave 0.1450 gram of AgI.

	Calculated for $C_9H_{10}O_2NI$.	Found.
I	43.64	43.77

2,5-Diiodbenzoic Acid.—Five grams of 2-amino-5-iodben-
zoic acid were added to a mixture of 50 cc. of concentrated
hydrochloric acid and 150 cc. of water. Some of the acid re-
mained undissolved. The whole was cooled with ice and
diazotized with 2 grams of sodium nitrite dissolved in a little
water. A colorless solution was obtained and to this was added
an aqueous solution of 13 grams of potassium iodide. A
dark green precipitate was formed when the mixture
stood in ice for one hour; it was gently heated and nitrogen
was evolved. The excess of iodine was removed by the ad-
dition of sodium bisulphite. The red precipitate remaining
after this treatment weighed 7.1 grams, which is the theo-
retical yield. The acid was purified by dissolving in dilute
ammonia and reprecipitating with hydrochloric acid. The
portion for analysis was further purified by crystallizing from
dilute alcohol. It formed slender prisms that melted to an
oil at 183°. It was very soluble in alcohol and ether and
moderately soluble in boiling benzene, from which it crys-
tallized in needles. It was insoluble in water.

0.1842 gram substance gave 0.2313 gram AgI.

	Calculated for $C_7H_4O_2I_2$.	Found.
I	67.92	67.85

The Sodium Salt.—2,5-Diiodbenzoic acid gave a sodium
salt which was very soluble in water. It crystallized from
concentrated solution when cooled with ice. A dilute aqueous

solution gave white precipitates with silver nitrate, lead acetate, and mercuric chloride. It gave a green precipitate with copper sulphate but did not give a precipitate with barium chloride. The precipitates were not changed in appearance by boiling in water.

Ethyl 2,5-Diiodbenzoate.—One gram of the acid was boiled for 6 hours in 40 cc. of alcohol containing 5 drops of sulphuric acid. The resulting solution was concentrated to a small volume and made neutral with ammonia and evaporated to dryness. The product was crystallized from alcohol. It formed colorless, silky needles, which melted at 65°. It was easily soluble in ether, benzene and hot alcohol.

0.2009 gram substance gave 0.2359 gram AgI.

	Calculated for $C_9H_8O_2I_2$.	Found.
I	63.18	63.51

2-Amino-3,5-diiodbenzoic Acid, $C_6H_2 \Big\langle \begin{matrix} COOH\ (1) \\ NH_2\ (2) \\ I\ (3) \\ I\ (5) \end{matrix}$.—At first
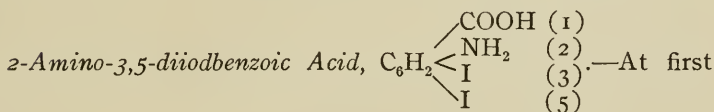
an attempt was made to prepare a diiodamino acid from the potassium salt of the above 5-iod-2-aminobenzoic acid by the direct action of iodine, in aqueous solution. When the materials were mixed in molecular proportions the action took place on warming on the steam bath. The product, instead of being an acid, however, proved to be 2,4,6-triiodaniline.

The desired acid was then obtained by the use of iodine monochloride. Five grams of 2-amino-5-iodbenzoic acid were dissolved in 200 cc. of 5 per cent. hydrochloric acid by the aid of heat. Four grams of iodine monochloride were then added to this solution. An immediate precipitate resulted and this increased by heating the mixture on a steam bath. The yield was 6.5 grams, which is 90 per cent. of the calculated. The product contained a trace of triiodaniline, which was removed by dissolving the precipitate in dilute ammonia, filtering and precipitating the acid with acetic acid. It was then purified by crystallizing from alcohol, whereupon it formed radiating

clusters of slender prisms that melted to a black oil at 230°–232°. It was very soluble in ether, difficultly soluble in hot benzene, and insoluble in boiling water.

o.1869 gram substance gave o.2262 gram AgI.

	Calculated for $C_7H_5O_2NI_2$.	Found.
I	65.23	65.40
N	3.60	3.54

It was found that 2-amino-3,5-diiodbenzoic acid could easily be prepared by the action of 2 molecular proportions of iodine monochloride on anthranilic acid. By this method the yields varied from 85 to 90 per cent. Five grams of anthranilic acid were dissolved in 100 cc. of 5 per cent. hydrochloric acid. Sixteen grams of iodine monochloride in 100 cc. of water were added and the mixture was heated on the steam bath for a few minutes. The precipitate weighed 12 grams and was found to be identical with the above diiodaminobenzoic acid.

Proof of Structure of the Diiodaminobenzoic Acid.—Five grams of the diiodaminobenzoic acid were dissolved in 15 cc. of concentrated sulphuric acid. The solution was cooled in a freezing mixture and 1.2 grams of powdered sodium nitrite were added. The mixture was poured on crushed ice and the resulting solution added gradually to 2 volumes of boiling alcohol by pouring through a condenser. The alcoholic solution was boiled for 15 minutes and poured into cold water when it gave a bulky white precipitate. This crystallized from alcohol in clusters and warts of fine prisms that melted at 235°. When mixed with a sample of *3,5-diiodbenzoic acid*,[1] prepared by Dr. Liddle, the melting point was not changed.

The Ammonium Salt of 2-Amino-3,5-diiodbenzoic Acid.— The crude, more or less colored, acid obtained by the action of iodine monochloride on anthranilic acid, was easily purified by means of the ammonium salt. When a solution of the acid in hot dilute ammonia was cooled, the ammonium salt

[1] This Journal, **42**, 505 (1909).

separated in long, slender crystals. These were easily soluble in warm water but difficultly in cold. When this salt is heated or dried over calcium chloride it dissociates and the product becomes insoluble in water. On acidifying the solution with acetic acid, 2-amino-3,5-diiodbenzoic acid was precipitated in a very pure state.

The *sodium salt* of 2-amino-3,5-diiodbenzoic acid was very soluble in hot water and moderately soluble in cold. It crystallized in slender prisms and a solution of this salt gave white precipitates with silver nitrate, mercuric chloride, lead acetate and barium chloride. A yellowish green precipitate was formed with copper sulphate. These precipitates were not changed when boiled with water.

2,3,5-Triiodbenzoic Acid.—Five grams of 2-amino-3,5-diiod-benzoic acid were dissolved in 15 cc. of concentrated sulphuric acid and 1.2 grams of powdered sodium nitrite were added in small portions. The mixture was kept cold with ice and after standing one hour was poured on crushed ice. The resulting solution was filtered to remove a small quantity of insoluble substance and the filtrate mixed with an aqueous solution of 5 grams of potassium iodide. The whole was then heated on the steam bath and the free iodine was removed by the addition of sodium hyposulphite. This treatment gave an orange-colored precipitate which weighed 5.7 grams, or 90 per cent. of the calculated. It was very soluble in hot alcohol and crystallized in radiating clusters of slender, colorless prisms that melted at 224°–226°. It was easily soluble in ether, difficultly soluble in boiling benzene and insoluble in hot water.

0.1489 gram substance gave 0.2105 gram AgI.

	Calculated for $C_7H_3O_2I_3$.	Found.
I	76.20	76.38

The *sodium salt* of 2,3,5-triiodbenzoic acid was easily soluble in hot and moderately soluble in cold water. It crystallized in clusters of slender prisms and its aqueous solution gave white precipitates with silver nitrate, barium chloride,

mercuric chloride, and lead acetate, and a green precipitate with copper sulphate.

2-Amino-3,5-diiodbenzoyl Chloride, $C_6H_2\Big\langle\begin{smallmatrix}COCl\ (1)\\ NH_2\ (2)\\ I\ \ \ (3)\\ I\ \ \ (5)\end{smallmatrix}$. — Ten
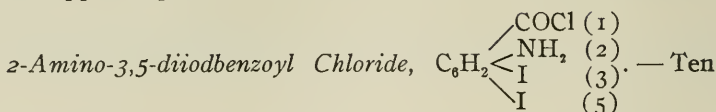
grams of powdered 2-amino-3,5-diiodbenzoic acid were suspended in 75 cc. of benzene, and 6 grams of phosphorus pentachloride added. The mixture was shaken from time to time until complete solution resulted. The reaction took place readily at the temperature of the room and was complete within an hour. The solution was filtered to remove a trace of suspended material and then used for the following experiments.

An attempt was made to obtain the chloride in a pure state by evaporating the benzene solution under diminished pressure at a temperature not exceeding 40°. This left a crust in the distilling bulb. Some dry ether was added and the evaporation repeated. The residue was very soluble in ether but in trying to crystallize it from ether and benzene it changed to a substance that did not dissolve in ether. As the crude chloride gave good results no further attempt was made to purify it.

2-Amino-3,5-diiodbenzamide.—A benzene solution of the chloride, made from 5 grams of the acid, was poured on 20 grams of powdered ammonium carbonate. The mixture was evaporated to dryness and the residue was washed with water. This treatment left 4.5 grams of gray crystalline material, which proved to be insoluble in dilute sodium hydroxide. It did not dissolve in water, chloroform o acetic acid. It was sparingly soluble in boiling alcohol and crystallized in long pointed needles. These began to decompose slowly at 230° and melted with decomposition at 238°–239°. They did not contain phosphorus.

	Calculated for $C_7H_6ON_2I_2$.	Found.
N	7.21	7.26

Ethyl 2-Amino-3,5-diiodbenzoate, C_6H_2
$$\begin{matrix} \diagup & COOC_2H_5 & (1) \\ & NH_2 & (2) \\ \diagdown & I & (3) \\ & I & (5) \end{matrix}$$
From
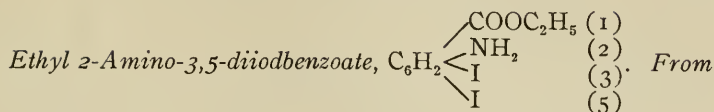
the Chloride and Alcohol.—A solution of 2-amino-3,5-diiod-
benzoyl chloride in benzene was mixed with ethyl alcohol
and the mixture was evaporated to dryness. The residue
was crystallized from alcohol and formed slender prisms that
melted at 101°.

From the Potassium Salt and Ethyl Iodide.—Three grams
of ethyl iodide were allowed to act on 3 grams of the potas-
sium salt of 2-amino-3,5-diiodbenzoic acid dissolved in 60
cc. of ethyl alcohol. The mixture was heated for 2 hours,
then the solution was evaporated and the residue treated
with dilute ammonia. The ester which remained insoluble
was crystallized from alcohol. It melted at 101° and was
identical with the ester obtained from the acid chloride, a
mixture of the substances obtained by the two methods melt-
ing at 101°. The yield of ester in this case was only about
32 per cent. On acidifying the ammonia solution used for
separating unaltered acid from the ester a precipitate of the
acid was obtained. The acid did not alkylate on the nitrogen.

0.2037 gram substance gave 0.2300 gram AgI.

	Calculated for $C_9H_9O_2NI_2$.	Found.
I	60.91	61.00
N	3.32	3.59

An attempt was made to alkylate 2-amino-3,5-diiodben-
zoic acid on the nitrogen by using four molecular proportions
of potassium hydroxide and eight of ethyl iodide to one of the
acid, as follows: Five grams of 2-amino-3,5-diiodbenzoic
acid were dissolved in 100 cc. of 95 per cent. alcohol contain-
ing 3 grams of potassium hydroxide. Sixteen grams of ethyl
iodide were added and the mixture was heated until it ceased
to give an alkaline reaction. This solution was evaporated
and the dry residue treated with ammonia. The yield was 2
grams of ester melting at 101°, and 3 grams of unaltered acid

were recovered from the ammonia solution. There was no evidence of alkylation on the nitrogen.

In another experiment 2 grams of the ester were dissolved in 15 grams of ethyl iodide, no other solvent being used. The solution was allowed to stand for four days at ordinary temperature. At the end of this time nothing separated and there was no evidence of any reaction. The ethyl iodide was allowed to evaporate spontaneously and the residue, without purification, melted at 99°. On recrystallization from alcohol it melted at 101° and was found to be unaltered ester.

$$\textit{2-Amino-3,5-diiodthiolbenzoic Acid,}\quad C_6H_2{\begin{cases} COSH & (1) \\ NH_2 & (2) \\ I & (3) \\ I & (5) \end{cases}}.\text{—A}$$
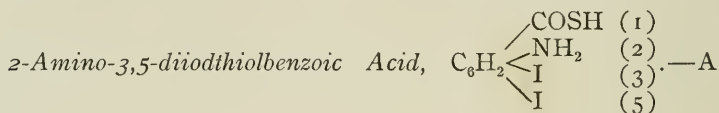
benzene solution of 2-amino-3,5-diiodbenzoyl chloride, made from 10 grams of 2-amino-3,5-diiodbenzoic acid, was slowly filtered into an alcoholic solution of potassium sulphydrate made by saturating a solution of 14 grams of potassium hydroxide in 100 cc. of 95 per cent. alcohol with hydrogen sulphide. The potassium sulphydrate solution was kept cold with ice and well shaken when the chloride was added. Potassium chloride separated. This was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in water and the solution acidified with hydrochloric acid. The product separated as an oil, but rapidly solidified, forming a red crystalline powder. This melted at 115°–116°.

Freshly prepared, it was readily soluble in chloroform or benzene, as well as in dilute ammonia and sodium hydroxide. Hydrochloric acid reprecipitated the thio acid from alkaline solutions. The substance, thus purified, melted at 116° with decomposition, leaving a yellow solid. The yield was 8.5 grams, or 85 per cent. of the calculated. The sample used for analysis was dried over sulphuric acid.

0.1969 gram substance gave 0.1171 gram $BaSO_4$.

	Calculated for $C_7H_5ONI_2S$.	Found.
S	7.90	8.16
N	3.45	3.38

The Disulphide of 2-Amino-3,5-diiodbenzoic Acid,
$[C_6H_2NH_2I_2COS]_2$.—Attempts were made to purify the thio
acid by concentrating a solution of the acid in chloroform on
the steam bath. This treatment produced a yellow com-
pound that decomposed at 202° and which would not dissolve
in chloroform. The same effect was produced by heating in
other solvents. When the thio acid was dried at 80° the
compound which decomposed at 202° was also produced.
This material did no dissolve in dilute ammonia or alkali.
Owing to this property and since the same substance was ob-
tained by treating the potassium salt of the thio acid with
iodine, we conclude that the compound is a disulphide. One
gram of the thio acid was dissolved in 20 cc. of water contain-
ing 0.14 gram of potassium hydroxide. To this solution 0.35
gram of iodine in 5 cc. of alcohol was then added. A yellow
precipitate was immediately obtained. This decomposed at
202° and had all the properties of the compound obtained by
heating the thio acid. It was almost insoluble in the common
organic solvents. The portion analyzed was then obtained by
dissolving the thio acid in chloroform and heating the solu-
tion.

0.1695 gram substance gave 0.1008 gram $BaSO_4$.

	Calculated for $C_{14}H_8O_2N_2I_4S_2$.	Found.
S	7.92	8.16

2-Amino-3,5-diiodbenzanilide was formed by the action of
hot aniline on the disulphide described above. The disulphide
at first dissolved in the excess of aniline, hydrogen sulphide
was evolved and slender prisms separated from the solution.
Alcohol was added and the residue filtered off. The product
was almost insoluble in hot alcohol or water, and did not dis-
solve in 10 per cent. sodium hydroxide. It began to char
slowly above 200° and melted to a black oil at about 224°.

	Calculated for $C_{13}H_{10}ON_2I_2$.	Found. I.	Found. II.
N	6.03	6.10	5.80

REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

XIII.—DERIVATIVES OF CYCLOHEXANE.

By E. P. Kohler and M. Cloyd Burnley.

It has been shown that many unsaturated ketones give both 1,2- and 1,4-addition products with organic magnesium compounds, and that the relative amounts of these products formed in any reaction depend on the nature of the magnesium compound as well as on that of the ketone. Most of the quantitative results published in previous papers were obtained by allowing a few organic magnesium compounds to react with a large number of typical α,β-unsaturated ketones. They show that the mode of addition to substances containing the chain $C:C.C:O$ is influenced more by the number and spatial character of the hydrocarbon residues in combination with the chain than by the chemical character of these groups.

We have found it much more difficult to determine the relation between the mode of addition and the nature of the magnesium compound. A summary of the results hitherto obtained with different reagents is shown in the following table, which gives the percentage of 1,4-addition product obtained by treating benzalmethylethyl ketone with various magnesium compounds:

CH_3MgBr	70
C_2H_5MgBr	71
$C_2H_5CH(CH_3)MgBr$	69
$C_6H_5CH_2MgBr$	68
C_6H_5MgBr	40

These results led to the conjecture that the mode of addition to any given ketone depends more on the chemical than on the spatial character of the hydrocarbon residue contained in the magnesium compound.[1]

The results obtained with derivatives of cyclohexane support these conclusions. They show that while cyclohexyl-

[1] This Journal, **38**, 520.

magnesium bromide gives, with typical ketones, even more 1,4-addition product than the simplest aliphatic magnesium compounds, the cyclohexyl group in benzalmethylcyclohexyl ketone prevents 1,2-addition to carbonyl as effectively as does the phenyl group in benzalacetophenone or the isobutyl group in benzalpinacolin.

<div align="center">EXPERIMENTAL PART.</div>

<div align="center">*I. Experiments with Cyclohexylmagnesium Bromide.*</div>

In the first experiments we used cyclohexyl iodide, as this had been used by earlier experimenters because they obtained a much better yield of the iodide than of the corresponding bromide.[1] The ease with which the iodide yields free iodine, however, proved so objectionable in the quantitative separation of the products that we decided to try the bromide. We found that by a slight modification of the procedure recommended by Freundler and Damon[2] it is possible to get a yield of more than 95 per cent. of cyclohexyl bromide from cyclohexanol.

Our procedure was as follows: Cyclohexanol was allowed to drop, very slowly, into 15 per cent. more than the calculated quantity of phosphorus tribromide that was cooled in a freezing mixture. The liquid was constantly shaken and the temperature kept well below zero until all of the alcohol had been added. The resulting mixture was left in a freezing mixture for several hours, then placed in an ice chest overnight, and finally kept at the ordinary temperature for two days. The product, purified as directed by Freundler and Damon, gave 92–97 per cent. of the calculated amount of pure cyclohexyl bromide.

Cyclohexyl bromide reacts readily with magnesium suspended in absolute ether, but the quantity of active magnesium compound formed is much less than the calculated amount. A part of the bromide loses hydrogen bromide and passes into cyclohexene, while some more of it is condensed to dodecahydrodiphenyl. As it was essential to prevent the formation

[1] Ber. d. chem. Ges., **35**, 2688; **40**, 4168.
[2] Compt. Rend., **141**, 593.

of complex products by having a sufficient excess of magnesium compound, we based our calculations on the assumption that only 50 per cent. of the magnesium is transformed into active magnesium compound, although a series of tests with benzaldehyde showed 70 to 75 per cent.

The method used for determining the relative amounts of 1,2- and 1,4-addition products, formed in the reaction between the magnesium compound and ketones, was essentially the same as that described in an earlier paper. The mixture of substances left when the reaction was complete was poured into iced acid, the salts removed with water, and the ethereal solution dried and partially distilled under a pressure of 20 mm. The residue left after removing everything that distilled when the liquid was heated to 100° under this pressure still contained all of the 1,2- and 1,4-addition products, along with hydrocarbons and other impurities.

For the purpose of destroying the 1,2-addition product the entire residue was dissolved in acetone and treated with potassium permanganate. The complete removal of unsaturated compounds without oxidation of any of the 1,4-addition product proved somewhat difficult, because the precipitated oxides of manganese, in the state in which they were formed at the ordinary temperature, protected large quantities of oxidizable material. To avoid this difficulty we adopted the following procedure, which gave satisfactory results: The permanganate was added in small quantities to the cooled solution until the length of time taken for reduction showed that little oxidizable material was left in solution. The vessel was then connected with an inverted condenser, heated for 15 to 20 minutes at the boiling point of acetone, and cooled again to the ordinary temperature before more permanganate was added. By repeating this process 3 or 4 times it was possible to destroy all unsaturated compounds, in the course of 3 or 4 hours, without using an unduly large quantity of solvent.

The method of oxidation left the oxides of manganese in a form in which they were easily separated by filtration and

washed with acetone. The filtrate was concentrated by distillation, then fractioned under diminished pressure. It yielded a small quantity of hydrocarbons, then some indifferent substances resulting from the oxidation of the 1,2-addition product (as, for example, methylcyclohexyl ketone from the addition product with benzalacetone), and finally—boiling at a much higher temperature—the saturated ketone resulting from 1,4-addition. The weight of this fraction was used in calculating the amount of 1,4-addition.

Reaction with Benzalacetone: *Phenylcyclohexylbutanone*, $C_6H_5CH(C_6H_{11})CH_2COCH_3$.—The ketone is a solid that separates from alcohol in colorless needles melting at 67°. It is readily soluble in ether, chloroform, acetone, and boiling alcohol; moderately in cold alcohol and ligroin. The yield was 37.2 grams from 36.4 grams of benzalacetone.

Analysis:

0.2185 gram substance gave 0.6667 gram CO_2 and 0.1817 gram H_2O.

	Calculated for $C_{16}H_{22}O$.	Found.
C	83.43	83.21
H	9.56	9.24

Reaction with Anisalacetone: *Anisylcyclohexylbutanone*, $CH_3OC_6H_4CH(C_6H_{11})CH_2COCH_3$.—The ketone is a colorless, viscous liquid boiling at 218° (18 mm.). The yield was 44 grams from 42 grams of anisalacetone.

Analysis:

0.1666 gram substance gave 0.4767 gram CO_2 and 0.1817 gram H_2O.

	Calculated for $C_{17}H_{24}O_2$.	Found.
C	78.46	78.02
H	9.23	8.97

Reaction with Benzalethylmethyl Ketone: *Phenylcyclohexylpentanone*, $C_6H_5CH(C_6H_{11})CH_2COC_2H_5$.—The ketone closely resembles the product from benzalacetone. It crystallizes

in colorless needles melting at 71°. The yield was 43 grams from 40 grams of unsaturated ketone.

Analysis:

0.1420 gram substance gave 0.4337 gram CO_2 and 0.1289 gram H_2O.

	Calculated for $C_{17}H_{24}O$.	Found.
C	83.61	83.3
H	9.84	10.0

Reaction with Benzalacetophenone: *Phenylcyclohexylpropiophenone*, $C_6H_5CH(C_6H_{11})CH_2COC_6H_5$.—A large part of the ketone separated as a solid when the ethereal solution of the magnesium derivatives was poured into iced acid. The solid was redissolved with addition of ether, the ethereal solution dried, freed from ether, and treated with permanganate, as in previous cases. The entire product from 20.8 grams gave 0.5 gram of benzoic acid. This represents only 5 per cent. of the unsaturated ketone, leaving 95 per cent. to be accounted for as 1,4-addition product. The amount of saturated ketone isolated in pure condition was somewhat less than this, because the mixture of the ketone with hydrocarbons and indifferent oxidation products that was left after most of the ketone had crystallized defied quantitative separation.

Phenylcyclohexylpropiophenone is sparingly soluble in alcohol, ether, and cold acetone. It was recrystallized from boiling alcohol, from which it separated in needles melting at 122°–122°.5.

Analysis:

0.1878 gram substance gave 0.5957 gram CO_2 and 1.1413 gram H_2O.

	Calculated for $C_{21}H_{24}O$.	Found.
C	86.30	86.51
H	8.21	8.36

II. Experiments with Benzalmethylcyclohexyl Ketone.

Preparation.—The unsaturated ketone was made by condensing benzaldehyde with methylcyclohexyl ketone obtained

by substituting cyclohexyl bromide for the chloride in the method of preparation devised by Bouveault.[1] For the purpose of condensation 10 cc. of a 10 per cent. solution of sodium hydroxide was added to a solution of 10 grams of the ketone and 8.4 grams of benzaldehyde in 50 cc. of alcohol. The solution was shaken in ice water while the hydroxide was added and afterwards kept in an ice chest for 10–12 hours. The separation of solid was then made as complete as possible by cooling in a freezing mixture, the solvent removed with a pump, and the solid washed—first with well-cooled alcohol, then thoroughly with water—and recrystallized from alcohol. The best yield was about 80 per cent.

Analysis:

0.1813 gram substance gave 0.5592 gram CO_2 and 0.1328 gram H_2O.

see errata p. 586

	Calculated for $C_{10}H_{18}O$.	Found.
C	84.11	84.10
H	8.41	8.13

Benzalmethylcyclohexyl ketone, $C_6H_5CH : CHCOC_6H_{11}$, is readily soluble in all ordinary organic solvents except ligroin. It crystallizes in colorless plates that melt at 58°. Dissolved in carbon bisulphide, it rapidly combines with bromine and forms a solid dibromide melting at 139°.

Phenylbutylcyclohexyl Ketone, $C_2H_5CH(C_6H_5)CH_2COC_6H_{11}$.— Benzalmethylcyclohexyl ketone was added to ethereal ethylmagnesium bromide in the usual way. The product reduced only a trace of permanganate, showing that there had been no addition to carbonyl. Distillation under diminished pressure gave a very pale yellow liquid that boiled at 188° (16 mm.). The color was evidently due to a slight impurity that could not be removed by distillation but disappeared on very brief exposure to sunlight.

Analysis:

0.1820 gram substance gave 0.5594 gram CO_2 and 0.1580 gram H_2O.

[1] Centralb., **1903**, II, 1437.

	Calculated for $C_{17}H_{24}O$.	Found.
C	83.60	83.82
H	9.83	9.64

Diphenylethylcyclohexyl Ketone, $(C_6H_5)_2CHCH_2COC_6H_{11}$.—
The product of the reaction between benzalmethylcyclohexyl
ketone and phenylmagnesium bromide gave a trace of benzoic
acid when treated with permanganate dissolved in acetone.
It, therefore, may have contained a small quantity of unsat-
urated alcohol due to 1,2-addition. The saturated ketone
formed by 1,4-addition boils at 250° (17 mm.) and melts at
68°. It is moderately soluble in alcohol and ether, readily
in acetone. Its solution in alcohol deposits it in long color-
less needles.

Analysis:

0.2056 gram substance gave 0.6500 gram CO_2 and 0.1468
gram H_2O.

	Calculated for $C_{21}H_{24}O$.	Found.
C	86.30	86.22
H	8.22	7.93

BRYN MAWR COLLEGE,
February, 1910.

AN EXTRACTION APPARATUS.

By NORMAN ROBERTS.

The apparatus herein described consists of a battery of
specially constructed extraction cells connected in series, to-
gether with an arrangement for evaporating, condensing and
circulating volatile solvents. There are also described two
varieties of supports designed for the convenient manipula-
tion of long and otherwise unwieldy series of extraction cells.
A search of catalogues and the literature shows no apparatus
closely similar to this, and it has been thoroughly tried out in
actual use and found to work well.[1]

[1] Ether extraction of corn meal in quantities of about 3 kg. per charge. The ap-
paratus once started ran without attention, often without notice, for several hours.
The loss of ether was slight, most of it being attributable to amateur construction of
the apparatus.

Jackson and Clarke[1] have recently described an extraction apparatus for use with large amounts of solid substances, which, however, does not provide for the use of cells in series, and in which the percolate is obtained through a muslin-covered tube.
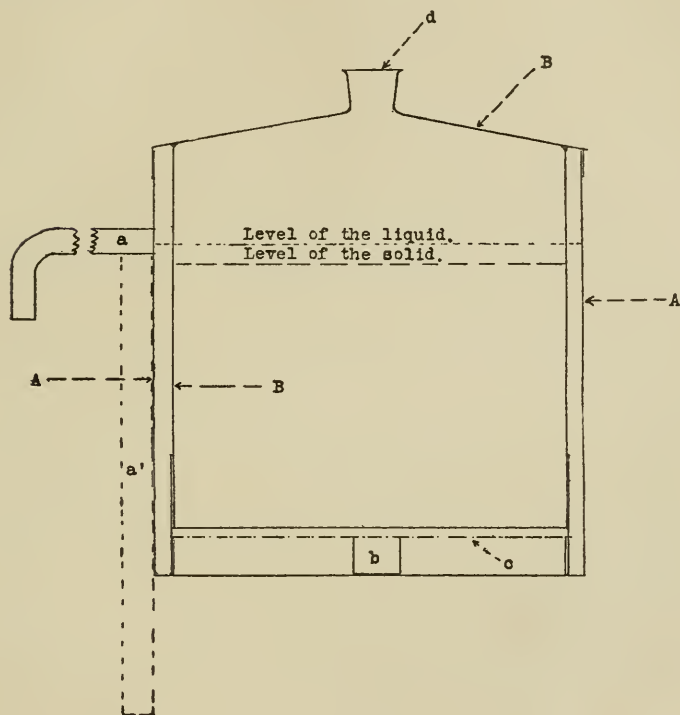
Fig. I.—The Individual Cell.

A, Outer container; B, inner container; a, overflow tube; a', position of overflow tube for vertical series; b, projecting leg at bottom of B; c, gauze bottom of B; d, mouth of B.

A number of ideas suggested themselves which we were not able to try in actual practice, as they required more mechanical skill and materials than were available. These untried ideas will be briefly described separately.

The individual extraction cell (Fig. I) is contructed as fol-

[1] This Journal, **42**, 287–291 (1909).

lows: The outer container, *A*, is cylindrical, with an overflow tube *a*, a short distance below the top. The inner container, *B*, which also serves as a lid, is of such a size as to leave a narrow space betewen it and the outer container. The lower surface of *B* is of fine gauze, and is removable, being supported by a metal rim which fits tightly over the lower end of *B* like the lid of a can. To prevent accidental obstruction of the current by the falling or sagging of the gauze bottom, there are three short projections pointing downward, around the edge of the bottom. The upper surface of *B* (which serves also to close in the top of *A*) has a mouth by which it is connected to the adjoining part of the apparatus. The overflow tube *a* is set near the top of the container, being above the level of the solid and slightly below the level of the liquid in the inner container. The overflow tube is best made of glass, in order that the rate of flow may be watched.[1]

The evaporator may be a glass flask with suitable connections, heated by hot water, or it may be a flat metal vessel heated by steam or hot water in a drum underneath, and provided with a feed opening, an escape pipe for vapor, a draw-off cock, and a glass gage, closed at the top with a cork. In suitable cases, either electricity or a flame may be used as the heating agent. The condenser (best a glass Liebig), bridges the interval from the top of the vapor tube to the upper opening of the highest extraction cell. A glass adapter at this point enables one to see how fast the liquid is circulating, and a second adapter at the same point serves for the introduction of fresh liquid as required. The second adapter is closed by a cork carrying a long glass tube of small diameter and thin wall, surrounded by ice or cold water in a larger tube, which equalizes the pressure within and without, with a minimum loss by the escape of vapor; moreover, this cork, not being too tightly introduced, blows out in case of a sudden considerable

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[1] In a large apparatus it would probably pay to have a cock at the bottom of the outer container, to drain it before cleaning out. In well constructed apparatus it would probably be feasible to free the exhausted solid from (volatile) solvents after draining, by blowing steam, best superheated, in a reverse direction, connecting the source of the steam to the overflow pipe, and the condenser to the mouth in the lid.

rise of pressure within. If the apparatus is well made, it should be possible to shut off the connection with the atmosphere entirely as soon as the apparatus is once fairly running.

The best materials are probably glass or tinned copper, each having its advantages and disadvantages. Inasmuch, however, as all parts of the extraction cell are accessible on
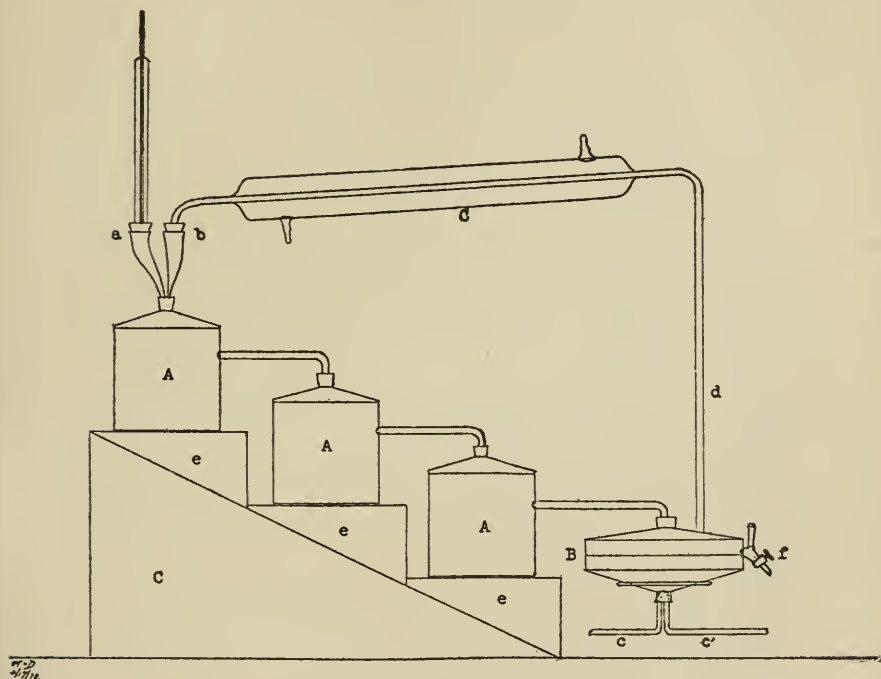
Fig. II.—Complete Apparatus (Oblique Form, with Support).

A, exterior cells; B, evaporator, lower half being the steam jacket; C, oblique support; a, adapter, with capillary tube, jacketed; b, adapter, from condenser; c, c′, steam inlet and exhaust pipes; d, vapor tube from evaporator; e, sliding supports for cells; f, drain cock and gage.

both sides for cleaning and drying, tinned iron may be used without much fear of rusting if reasonable care be taken.

Operation.—It will be noted that the apparatus contains no filtering or straining layer—no cotton packing, sand, etc. The single layer of gauze serves merely to keep the *mass* of

powder in place, clarification being effected by sedimentation as the percolate slowly rises in the space between the inner and outer containers. Filtration, if ever necessary, is best done outside of the cell. Owing to the absence of passive obstruction, all the excess of liquid in the apparatus accumulates in the lowest part of the circuit, namely, in the evaporator, and the rapidity of the circulation is dependent entirely on the rate at which heat is applied to evaporate the solvent. Freshly charged cells are introduced at the lower end of the series. Charging a cell of this kind is a much simpler matter than charging an ordinary percolator, as no special packing or great amount of skill is required. If the powder does not swell on wetting, it is charged dry; if it does swell, it is given an opportunity to do so before being charged. In charging, the inner container is inverted, the gauze bottom removed, the proper amount of powder introduced (it must be entirely submerged during extraction), the gauze replaced, and the whole (inner container) allowed to settle slowly into the proper amount of liquid previously introduced into the outer container. It is often advantageous to combine maceration with percolation, by alternately circulating the solvent and letting it rest, which can be done, *e. g.*, by turning the heat and water to the condenser on during the day, and off during the night, or during other proper intervals.[1]

It is, of course, possible to use a single extraction cell only, but a series, even of two, is far preferable, by reason of increased rapidity and completeness of extraction. Too long a series necessitates the use of too much liquid (especially, for example, of ether) and is unwieldy and labor-consuming; but under suitable conditions (as when the percolate cannot be heated), a long series gives ideal results, especially as to saturation and therefore uniformity of percolate and the exhaustion of the powder or other matter being extracted.

A lute of glycerol and kaolin is of great service in extraction with ether.

[1] It is possible, but rather dangerous, to leave this *or similar apparatus* running all night. When no one is within hearing distance, it is preferable to trust to the slower but safer process of maceration in any extraction with volatile and inflammable solvents.

The Support.—Probably the chief reason for the unpopularity of long-series percolation on the small scale is the trouble of changing the cells. Unless all joints are *perfectly* tight (a difficult condition), pressure, as a means of circulating the liquid, is out of the question, and gravity must be relied on. This necessitates a step- or ladderlike support, with a stepping up of each cell and its disconnection and reconnection to both of its neighbors. With only two or three cells in series, this is little extra trouble, but the work soon becomes prohibitive as the number of cells in series increases. But by the use of sliding supports the series can be moved up *en masse* when the top cell is to be removed and a fresh cell introduced at the bottom. The guide on which the supports slide may be vertical or inclined; in either case, a separate sliding base will be needed for each cell. In the vertical form the guide is a rod (gas pipe), the sliding bases being L-shaped wooden pieces, the vertical limbs of which slide on the guide, which fits in a deep groove and is held on by a catch, while the horizontal limb supports the cell. In the oblique form the guide is an inclined plane, and the sliding bases are steplike platforms. The vertical form needs little desk room, and is convenient for small cells in not too long series. The oblique form would seem to be useful for long series of large cells. I have tried the vertical form with good results. The oblique form is as yet only on paper, since I have never worked with large cells in series of more than two.

The following suggestions are due to my assistant, Mr. F. Alex. McDermott, who has helped make the apparatus and has done most of the work of operating it:

Where the most rapid and efficient working is desired it is best to have at least one more cell than the number required to make up the battery. The extra cell or cells stand charged and macerate while the battery is percolating, each cell being cleaned and recharged as soon as it is removed exhausted from the upper end of the battery. When a fresh cell is needed, the cell which has stood macerating longest is connected in at the bottom, and the exhausted cell at the top removed,

and percolation is thus continued with the minimum of interruption.

If the apparatus is constructed of metal, it is desirable to use the same metal throughout, to avoid possible electrolytic effects.

The heat applied to the evaporator should be as constant as possible; sudden accessions of heat (absolute or relative) cause corresponding increases of pressure in the system; if extreme, this phenomenon may be practically an explosion. This is one reason (probably the best) for turning off the heat at night or at other times when the apparatus cannot be watched.

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NOTE ON THE REACTIONS OF DIAZOALKYLS WITH 1-PHENYL-2-METHYLURAZOLE.

By Sidney Nirdlinger, E. K. Marshall, Jr., and S. F. Acree.

In the article in the April number of This Journal,[1] $\frac{K_{trans}}{K'_{trans}}$, line 11, p. 361, should be $\frac{C_2}{C_3}$. This oversight does not occur in the fuller discussion in the succeeding pages.

· On p. 367 it is not stated that the experiments by Mr. Marshall with diazoalkyls were *not* performed at 25°; as stated on p. 363, line 8, his work is being done at *lower* temperatures, 0° and —70° at present. Under these conditions only does the ratio of esters obtained when the acid is freshly liberated from the salt differ at all from that found when the acid is allowed to change with time. Whether this change is due to a rearrangement of two or more tautomeric forms, as we believe, or to slow ionic changes, salt formation, polymerization, etc., is being investigated. It may be mentioned here that Mr. Marshall finds that the ratios, *N*-ester : *O*-ester, obtained from the silver salt of 1-phenyl-2-methylurazole

[1] Vol. **43**, p. 358.

and methyl iodide in 40 per cent. alcohol are approximately the same, whether the silver salt be *suspended* or *dissolved*.

Mr. Marshall has further found that the ratios *N*-ester : *O*-ester, obtained from the sodium, zinc and silver salts at —70°, when the 1-phenyl-2-methylurazole is liberated by hydrochloric acid from the salts in alcoholic-ether solutions in the presence of diazomethane, are all practically the same, about 87 : 13. The 1-phenyl-2-methylurazole in alcoholic ether solutions at 20°, 0°, or —70° gives a ratio 94 : 6. This shows that these salts all have about the same equilibrium constants, which are slightly different from those for the acid. The mass law requires that the ratios of keto to enol ions be the same for all salts and the acid in dilute solutions. Whether this difference between the equilibrium constants for the acid and for the salts is due to a difference in the dissociation constants, and to a difference in the ratio of molecular keto and enol forms, or to an apparent change in the ratio of the keto and enol ions because the ordinary dilution formulas do not hold in the rather concentrated solutions used, or to other causes, is being investigated. We have made the very important observation that the silver salt has apparently about the same equilibrium constants as the other salts. The higher percentage of *O*-ester which we have obtained from the silver, mercury and lead salts and alkyl halides may be, to some extent, due to *a reaction of the undissociated*[1] *salt, which we have several times discussed as possible,* or to other causes. Mr. Marshall is investigating this subject fully.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, April 8, 1910.

OBITUARY.

HANS LANDOLT.

With the passing away, on March 15th, of Landolt, nearly the last of the old school of physical chemists is gone. This school had for its aim the study of the physical properties of chemical compounds. The members of this school, of

[1] THIS JOURNAL, **38**, 260–1; Ber. d. chem. Ges., **41**, 3210, 3214, etc.

whom we need mention only Gladstone and Perkin in England, and Kopp and Landolt in Germany, lived in that period when chemical compounds were made by the thousand. This applies especially to organic compounds, the incentive being for a long time the fertile theory of Kekulé.

As these compounds were brought to light, it became desirable to know their physical properties, and these were studied with a degree of thoroughness and comprehensiveness which must always arouse the admiration of men of science. Take, for example, the work of Kopp on the boiling points of liquids, of Perkin on magnetic rotation, and of Landolt on refractivity, optical activity, etc.

Hans Landolt was born December 5th, 1831, in Zurich. His earliest work in chemistry was done at the University of Zurich under Loewig. When the latter was called to Breslau young Landolt followed him there and obtained from this institution the degree of Doctor of Philosophy in 1853, his dissertation being upon "Arsenic Ethyl."

From Breslau, Landolt went to Berlin to study with Rose and Mitscherlich, and then to Heidelberg, to work with Bunsen. He returned to Breslau in 1856 as privatdozent, and in 1867 was appointed full professor in Bonn. Two years later he accepted the professorship of chemistry and mining at the Technical High School in Aix-la-Chapelle. In 1880 Landolt accepted the professorship at the newly opened Agricultural High School in Berlin, and in 1891 succeeded Rammelsberg as director of the II Chemical Institute at the University of Berlin. This position he held until he retired in 1905.

The most important lines of work with which the name of Landolt will always be connected are the following:

From his study of the molecular refraction of organic compounds he arrived at the formula connecting the index of refraction with density, which is the simplest and the best expression of this relation, even at the present time.

One of his best known investigations is in connection with the optical activity of organic compounds. He made

an exhaustive study of the effect of the solvent, of the temperature, etc., on this property, and greatly improved the apparatus used in measuring optical rotation. His book dealing with optical activity, "Optisches Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen," is *the* authority in this field. Landolt's work on the melting points of organic compounds is not as well known as those lines of investigation referred to above, but shows that love of accuracy which characterized everything that he did.

The investigation for which Landolt is best known to the younger generation of physical chemists, or the so-called new school of physical chemists, is that which has to do with the fundamental question whether the law of the conservation of mass holds rigidly when chemical reactions take place? The question to be answered experimentally was whether weight remains constant during chemical reaction. Do the products of a chemical reaction weigh the same as the substances that entered into the reaction?

The writer had the good fortune to see in progress, in 1893, this work which was carried on for nearly twenty years.

The first part of the problem was to secure a fine balance, and Landolt had constructed for this work the finest chemical balance that the world had ever seen. This was but the beginning. Every possible precaution against changes in temperature, mechanical disturbance, and the thousand and one other disturbing effects was adopted and with such skill, that this investigation alone places Landolt in the very first rank of careful workers.

At first Landolt found changes in weight that were larger than could be accounted for by experimental errors. He, however, continued this very exacting investigation even after he retired from active professional work, and lived to furnish a perfectly satisfactory explanation of the changes in weight that he had found. They were due to changes in the volume of the vessels containing the reacting substances, caused by small changes in temperature.

By the death of Landolt chemistry loses one of her most careful investigators, and those who knew him lose a kind-hearted, generous and sympathetic friend—a man who lived for a scientific ideal. H. C. J.

REPORTS.

INDUSTRY AND ANALYSIS OF THE FATS.[1]

The chemistry and modern industry of the fats originated in France. It is, in fact, on the shores of the Mediterranean that the cradle of the discovery of soap and, consequently, of saponification, the fundamental operation in the chemistry of the fats, must be sought. Whether the Arabs, who, thanks to the discovery of the chemical action of quicklime on the ashes of saliferous plants, knew how to prepare a hard soap from olive oil, taught this art to the people of Marseilles, or whether the latter learned it from the Genoans, it is a well-established fact that in the 11th century the art of the soap maker enjoyed a high reputation at Marseilles and reached such a degree of perfection that for several centuries "Marseilles soap" held the first rank among all the world's soaps.

The lure of gain having soon led to fraud by the introduction into soap of an excessive quantity of water, a practice which analysis alone could expose, the detection of fraud by means of chemical analysis became necessary. The analysis of soap originated in France as early as the 18th century and it was Claude Joseph Geoffroy who, probably in the course of such an analysis, made the important observation that the fatty substance separated from soap by the action of hydrochloric acid was clearly distinguished from natural fats by the ease with which it dissolved in alcohol. It appears that his contemporaries were in no wise ignorant of this observation. Three years later, in 1745, Macquer recognized that the greater solubility in alcohol of rancid fats is due to the presence of an acid substance, and he found that the solubility increased directly as the quantity of free fatty acids.

The discovery of fatty acids was thus made. As seen from the point of view of our present knowledge, the discovery of glycerol by Scheele, in 1783, ought to have furnished the key to the constitution of the fats, but the science of chemistry was not yet sufficiently advanced. Scheele regarded the fats as compounds of carbonic acid, water, and phlogiston.

[1] Address delivered before the Société Chimique de France, April 3, 1909, and published in Bull. Soc. Chim. of May 20, 1909.

The solution of the problem was reserved for the genius of Chevreul who brought light and cleared up the darkness in which the chemistry of the fats was then buried. The immortal researches of Chevreul, the establishment of the industry of the fatty acids which immediately resulted from them, and the brilliant succession of investigations by Berthelot and by Wurtz, who confirmed, consolidated, and elaborated the views of the master, are too well known by every one to need being traced again in this rapid retrospective review.

It is therefore rather the modern development of the chemistry and industry of the fats, the exposition of which the Council of the Société Chimique has been kind enough to confide to my feeble efforts, which will take up our attention to-day.

It had, to be sure, been recognized that the natural fats consist exclusively of triglycerides; the mono- and diglycerides, whose properties had been made known through the beautiful syntheses of Berthelot, had not been found in natural fats. The only apparent exception to this general rule, furnished by the presence of dierucin in some old oils of colza, is easily explained, as we shall see later, by the fact that the oils had become rancid.

The various known fatty acids must give rise to as many different triglycerides, resulting from the combination of a molecule of glycerol with three identical acid radicals. We shall call them *simple glycerides*.

The number of simple glycerides being limited by the number of known fatty acids, chemists could not, for a long time, explain the differences exhibited by fats and oils apparently containing the same fatty acids otherwise than by assuming varying proportions of the corresponding triglycerides. Berthelot, nevertheless, had, as early as 1860, expressed the opinion that the complexity of the natural fats might be explained by the existence of compounds in which one molecule of glycerol was combined with the radicals of two or three different acids. Glycerides of such a composition would be called *mixed glycerides*.

To make clear the ideas on this point, it is well to bring together the different possible combinations in the following scheme:

$$C_3H_5 \begin{cases} OR \\ OR \\ OR \end{cases}$$

Simple triglyceride.

$$C_3H_5 \begin{cases} OR'' \\ OR' \\ OR'' \end{cases} \quad C_3H_5 \begin{cases} OR' \\ OR'' \\ OR'' \end{cases} \quad C_3H_5 \begin{cases} OR' \\ OR'' \\ OR''' \end{cases} \quad C_3H_5 \begin{cases} OR'' \\ OR' \\ OR''' \end{cases} \quad C_3H_5 \begin{cases} OR' \\ OR''' \\ OR'' \end{cases}$$
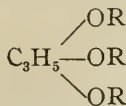
Mixed triglycerides.
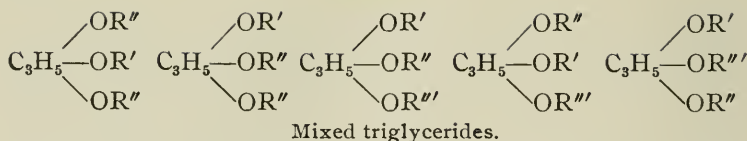
Although quite a large number of simple triglycerides were known in pure state—tributyrin having been prepared as early as 1844 by Pelouze and Gélis—it is only within the last ten years that it has been possible to extract from a natural fat a true mixed triglyceride. Oleodistearin, discovered by Heise, opened the series; there then followed, in perhaps too rapid succession, palmitodistearin, stearodipalmitin, myristo-palmito-olein, dipalmito-olein, and dioleostearin (whose existence is still doubtful), and a few other mixed glycerides, put forward as chemical individuals but to-day abandoned as not existing.

The difficulty of isolating such chemical individuals in pure state is considerable; this is perhaps due to the intramolecular changes which mixed glycerides suffer during the treatment with solvents. But the conviction that mixed glycerides form the larger proportion of the natural fats will be borne upon us when we recall the laborious experiments of Bömer, according to whom beef and mutton tallow contain no more than 1.5 to 3 per cent. of tristearin, a result demonstrated by a very large number of crystallizations from various solvents.

Thanks to the elaboration of Berthelot's classical methods, much work has been done in the preparation of mixed glycerides. To-day more than a score are known, the simplest of which is acetodiformin, prepared by Béhal. From the formulas given above, it follows that with two different acid radicals two isomers are possible, and that if all three acid radicals are different three isomers can exist. When the number of known fatty acids is considered, it will easily be seen that the number of different triglycerides whose existence in natural fats is possible must be enormous. In order to calculate their number, Berthelot gave formulas which Kablukow has developed; but although indicating an extraordinary number, amounting to thousands, of possible combinations, these formulas do not represent all the isomers predicted by the theory. Let oleic acid be replaced by its isomer, elaidic acid, or erucic acid by brassidic acid, and the number of mixed glycerides containing these acids will be doubled and quadrupled. Assume racemic combinations such as those repre-

sented by the last four formulas, let these be split up into two opposite optical isomers—without prejudice, however, to the optical activity due to the acid radicals themselves—and the number of mixed glycerides will again be doubled. We shall not expatiate on this prodigious multiplicity and shall not even try to evaluate it. We have as yet reached only the preliminary stage in the work leading to the clear resolution of the different glycerides which constitute any one oil or fat.

It might be thought that one means which, if not quite simple, could at least be used for determining the composition of these apparently irresolvable mixtures, would consist in extracting from them, by repeated crystallizations, individuals whose properties could be compared with those of compounds prepared synthetically; recourse would then be had to elementary analysis. But such is not the case, for the differences between the percentages of carbon, hydrogen, and oxygen are too small to furnish useful indications. We might perhaps turn to the melting point, a constant so characteristic for pure organic substances. Unfortunately, the mixed glycerides present the phenomenon of double melting point in a manner even more deceptive than the simple glycerides. Abandoning the hypothesis of the existence of two modifications, pointed out some fifty years ago by Duffy and by Heintz, it was sought to explain this curious property by the phenomenon of superfusion of the melted substance cooled below its freezing point and not yet returned to its normal crystalline state. The original hypothesis has recently acquired new life, thanks to the almost simultaneous, independent investigations of Grün and Schacht and of Bömer. The experiments of these authors have shown that the mixed glycerides can be obtained in two forms, *viz.*, an unstable and a stable modification. By inoculating the unstable fat with a crystal of the stable modification, the former is gradually converted into the stable form, characterized by a melting point higher than that of the unstable modification. The latter has the lower melting point, called the "first melting point," or, following Bömer's suggestion, the "transition point." The compounds obtained in crystalline form have but a single melting point, the higher. It is the modification which cannot be converted into its unstable isomer by the inoculation method. The "true melting point" should therefore be assigned to the crystalline forms. It is at all events certain that there exist two forms, but the cause of this cannot yet be explained. Is the existence of these two forms due

to a polymerization? The determination of their molecular weights by the freezing and boiling point methods has furnished no decisive indications on this subject. Perhaps the unstable modification is one of those liquid, anisotropic phases described by Wallerant and Jaeger, a hypothesis which becomes more probable when we consider the fact that the melting points vary irregularly when the substances are allowed to stand for longer or shorter periods of time. Here are phenomena which offer a vast field for investigation and, consequently, for discoveries. Without exaggeration, it can be said that there is enough work here for a whole army of investigators.

We shall confine ourselves here to the consideration of the mixed glycerides containing three organic acid radicals. Mixed glycerides with organic and mineral acid radicals are beyond the scope of our study. But it is meet to consider briefly, in passing, a very remarkable mixed glyceride containing the radicals of phosphoric acid and of two fatty acids; I refer to lecithin, a natural principle found in the yolk of eggs, milk, the retina of animals of the bovine genus, the grains of maize, peas, the gluten of wheat; in sum, a fat seeming to play an important rôle, still ill defined, in the economy of the animal and vegetable organism. We see here an important point of contact between the pure and applied chemistry of the fats and their physiological chemistry.

Moreover, we shall return to this point frequently in the course of this address.

We know that the most important chemical reaction of the fats is saponification, or, in scientific language, hydrolysis.

The splitting up of the glycerides into glycerol and fatty acids is not a tetramolecular reaction such as treatises on general chemistry represent by the equation

$$C_3H_5{\begin{smallmatrix}\diagup OR \\ —OR \\ \diagdown OR\end{smallmatrix}} + 3H—OH = C_3H_5{\begin{smallmatrix}\diagup OH \\ —OH \\ \diagdown OH\end{smallmatrix}} + 3R—OH.$$
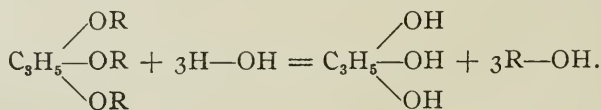
It takes place in three consecutive phases, which may be represented by the three following equations:

$$(1a)\ \ C_3H_5{\begin{smallmatrix}\diagup OR \\ —OR \\ \diagdown OR\end{smallmatrix}} + H—OH = C_3H_5{\begin{smallmatrix}\diagup OH \\ —OR \\ \diagdown OR\end{smallmatrix}} + R—OH\ ;$$

$$(1b) \quad C_3H_5 {\Large <}^{\text{OH}}_{\text{—OR}}_{\text{OR}} + H{-}OH = C_3H_5 {\Large <}^{\text{OH}}_{\text{—OH}}_{\text{OR}} + R{-}OH;$$

$$(1c) \quad C_3H_5 {\Large <}^{\text{OH}}_{\text{—OH}}_{\text{OR}} + H{-}OH = C_3H_5 {\Large <}^{\text{OH}}_{\text{—OH}}_{\text{OH}} + R{-}OH.$$
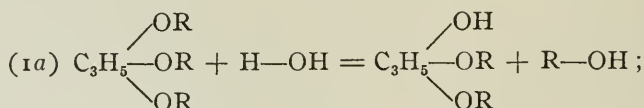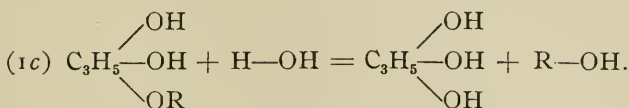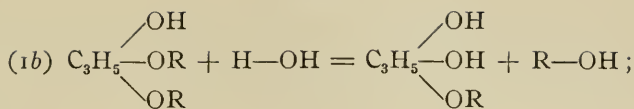
From the triglycerides we pass to the diglycerides, then to the monoglycerides, ending up finally with the products of complete hydrolysis. This way of looking at the fundamental reaction in the chemistry of the fats has been criticized by several chemists, but it has been verified by numerous experiments, purely chemical as well as physico-chemical. It has been shown in an almost irrefutable manner that hydrolysis takes place in three phases. Thanks to this agreement between the chemical and physical evidence, the general equation,

$$C_3H_5(OR)_3 + 3H{-}OH = C_3H_5(OH)_3 + 3R{-}OH,$$
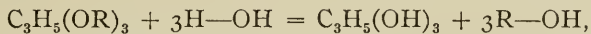
must be considered as the resultant of the three equations given above, each of the latter representing a bimolecular reaction.

It cannot be expected that these three phases should succeed each other consecutively in an absolutely distinct manner, nor can it be hoped to find the total mass of the triglycerides at first completely and exclusively decomposed and transformed into diglycerides according to equation (1*a*), then this mass of diglycerides transformed completely into monoglycerides according to (1*b*), and lastly the monoglycerides finally split up into glycerol and free fatty acids. We must rather expect to find the three phases represented in the equations above taking place simultaneously and concurrently, so that at the same moment one molecule of diglyceride may be transformed into a monoglyceride and a fatty acid, one molecule of monoglyceride be decomposed into glycerol and a fatty acid, while one molecule of triglyceride may still remain intact or undergo the first phase.

Hydrolysis does not take place in the absence of water. The latter must therefore be considered as the hydrolyzing agent, whether it be used alone or with catalytic agents, such as bases, acids, or enzymes.

At ordinary temperatures water alone acts extremely slowly on glycerides; in fact, at ordinary temperature, in the absence of favorable conditions (such as the simultaneous presence of light and of atmospheric oxygen), the hydrolysis would be almost *nil*. It will be recalled that Friedel found unchanged triglycerides in fats from the tombs of Abydos, the existence of which goes back several thousands of years. But let the temperature of the water be raised to 220°, and almost complete hydrolysis will be effected. That is the principle of the Tilghmann process, perfected by Hughes, which has been put into operation on an industrial scale in one of the stearin factories of Paris.

The saponification by caustic potash and soda had been carried on for centuries, but it had never been recognized that this operation consists of two clearly distinct chemical reactions. First phenomenon: hydrolysis of the fat, the alkali acting only as an accelerator or catalytic agent. Second phenomenon: formation of soaps by the union of the fatty acids with the alkali. The alkali always being present in excess, the two reactions take place almost concurrently and were regarded as consisting of but a single reaction. It is only since the creation of the industry of the fatty acids that the clear distinction between the two consecutive phases has become well understood by the soapmaker.

If we admit as being correct the point of view that the caustic alkalies are accelerating or catalytic agents, it follows that it is not necessary to use at least molecular proportions of these bases relatively to the fatty acids set free by complete hydrolysis. The greater the proportion of bases present (allowance being made for the chemical affinity or the accelerating power of the different bases), the more rapidly must the hydrolytic resolution of the glycerides be effected and the greater must be the quantity of salts of fatty acids formed. But the use of a quantity of bases smaller than would be necessary to neutralize the fatty acids produced by complete hydrolysis ought not to prevent the decomposition into glycerol and fatty acids from being completely effected. This, evidently, is not the process employed industrially with the caustic alkalies; but there is no doubt that, under pressure, complete hydrolysis could be effected with a proportion of alkali insufficient to neutralize the fatty acids formed.

Let us verify the correctness of our views by studying the saponification of fats by quicklime: The theoretical quantity of caustic lime necessary for the saponification of a fat whose mean molecular weight is 860 is 9.7 per cent.

Unless the proportion of lime is increased to 12–14 per cent., complete hydrolysis of the fat cannot be effected in an open vessel, *i. e.*, under atmospheric pressure and at a temperature of 100°–105°. But let the pressure be raised to 12 atmospheres, which corresponds to a temperature of about 190°, and 1 per cent. of lime will be sufficient to effect practically complete hydrolysis. This quantity of lime is converted into a calcium soap by a subsequent reaction. We should lay stress on this fact, that in using lime as an accelerator we have lowered considerably the temperature necessary for complete hydrolysis by means of water alone. Magnesia and zinc oxide behave like lime.

Thanks to the investigations of Chevreul and of Fremy, it had been recognized that concentrated sulphuric acid can likewise effect complete hydrolysis of fats. We prefer to say that sulphuric acid behaves like a catalytic or accelerating agent. If a fat is heated at 120° with 4 per cent. of concentrated sulphuric acid and the mass is kept stirred by a current of steam, hydrolysis is effected in about ten hours. This is shown in the following table:

Table I.—Tallow Hydrolyzed at 120° with 4 Per Cent. of Sulphuric Acid (Lewkowitsch.)

Sample taken after	Free fatty acids. Per cent.	Sample taken after	Free fatty acids. Per cent.
1 hour	42.1	6 hours	91.7
2 hours	65.1	7 "	91.7
3 "	79.3	8 "	92.3
4 "	83.7	9 "	93.0
5 "	88.6		

The sulphuric acid acts in the first place through the formation of sulphonated compounds of the glycerides, forming a perfect emulsion with water and thus favoring the intimate contact between the hydrolyzing water and the globules of the nonsulphonated fats which are divided, pulverized, so to speak, by the steam. The accelerating action of the acid would thus be explained. On the other hand, dilute sulphuric acid, not being able to form sulphonated compounds, ought not to act as a catalytic agent, and hydrolysis should decrease progressively as the concentration of the sulphuric acid diminishes. This is quite in harmony with the facts, as is shown in Table II.

Table II.—*Hydrolysis of Tallow Containing 6.2 Per Cent. Free Fatty Acids with 4 Per Cent. of Sulphuric Acid of Different Concentrations (Lewkowitsch).*

Per cent. of fatty acids after action of steam for T hours.

Per cent. H_2SO_4 in acid.	$T=1.$	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
98	42.1	65.1	79.3	83.7	88.6	91.7	91.7	92.3	93.0	92.3	93.0
90	37.2	47.7	57.6	65.1	72.5	76.0	80.0	81.8	83.6	86.2	88.0
85	34.1	45.2	50.8	62.6	68.2	73.1	75.0	76.2	79.4	84.3	84.9
80	31.6	45.2	57.6	65.1	73.1	75.4	79.3	80.6	83.7	85.5	87.4
70	15.5	16.7	17.9	18.3	18.6	20.3	24.8	26.5	28.5	31.0	32.6
60	6.2	6.2	6.2	6.2	…	…	…	…	…	…	…
50	6.2	6.2	6.2	6.2	6.8	…	…	…	…	…	…

Per cent. H_2SO_4 in acid.	$T=12.$	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.
98	93.6	93.6	93.0	93.6	93.6	…	…	…	…	…	…
90	86.8	88.6	88.6	89.0	90.5	90.5	…	…	…	…	…
85	89.3	89.3	89.3	89.9	89.9	89.9	…	…	…	…	…
80	88.6	89.0	89.9	89.9	89.9	…	…	…	…	…	…
70	34.7	35.4	37.0	39.0	40.1	42.7	45.2	46.5	47.7	47.7	47.7

Table III.—Hydrolysis of Oils and Fats with Twitchell's Reagent (Lewkowitsch).

(100 grams of oil or fat subjected to the action of steam with 1 per cent. of sulpho aromatic compounds in open vessels.)

oil or fat.	Original acid number.	Acid number after T hours.								
		T = 2.	7.	9.	12.	14.	16.	18.	20.
Cotton	5.67	8.75	61.28	99.8	129.4	137.6	148.7	150.1	155.9
Whale	6.01	14.99	48.69	63.72	72.42	80.8	84.31	85.82	89.68
Colza	2.16	8.4	23.24	30.59	44.26	50.57	53.6	55.4	56.58
Lard	2.6	1.37	38.66	58.73	82.42	90.81	98.49	107.3	107.9
Tallow	11.15	5.03	25.68	43.44	49.39	50.11	52.03	53.1	53.85
Cocoa	18.75	114.0	221.4	232.9	233.2	236.0	236.2	237.2	237.9

oil or fat.	T = 22.	24.	26.	28.	30.	32.	34.	36.
Cotton	157.9	161.4	164.5	165.2	166.3	167.0	168.4	168.9
Whale	90.71	91.67	91.67	91.7	94.69	97.88	98.07	98.9
Colza	56.72	57.91	59.58	60.6	61.46	61.61	61.87	62.3
Lard	109.0	110.5	112.0	115.2	118.3	118.6	119.1	120.2
Tallow	55.6	57.11	59.82	60.23	63.95	66.2	67.3	68.5
Cocoa	238.9	239.5	239.8	239.8	240.6	240.9	241.0	241.2

We see that, beginning with 60 per cent. sulphuric acid, hydrolysis ceases completely.

The chemical action which sulphuric acid exerts on unsaturated acids is, moreover, not contrary to our views; it is a secondary reaction comparable to the formation of a calcium soap in the process of water hydrolysis accelerated by lime.

This is shown clearly by the action of Twitchell's reagent, a sulphostearo aromatic compound obtained by the action of concentrated sulphuric acid on a mixture of oleic acid and aromatic hydrocarbons, such as benzene or naphthalene.

One to 2.5 per cent. of this reagent is sufficient to effect, in a given time, almost complete hydrolysis of fats heated in a current of steam at ordinary pressure, especially in the presence of a few per cent. of free fatty acids.

In Table III are given the results of a series of experiments carried out in the laboratory with a commercial reagent.

Experiments carried out with reagents prepared from naphthalene, anthracene, and phenanthrene, are summarized in Table IV:

Table IV.—Hydrolysis of Cotton Oil with 1 Per Cent. of Sulphostearo Aromatic Compounds (Lewkowitsch).

(a) Neutral oils.

Compound with	Original acid number.	6.5 h.	13 h.	19.5 h.	26 h.	32.5 h.	39 h.	45.5 h.
Naphthalene	1.22	146.7	190.7	201.4	211.4	...	...	...
Anthracene	1.22	2.5	21.8	76.3	170.7	186.5	190.7	...
Phenanthrene	1.22	45.7	125.7	177.7	183.6	194.1	201.2	...

(b) Oils containing free fatty acids.

Compound with	Original acid number.	6.5 h.	13 h.	19.5 h.	26 h.	32.5 h.	39 h.	45.5 h.
Naphthalene	8.3	30.9	194.1	216.9	210.7	...	...	...
Anthracene	8.3	15.01	60.5	112.4	147.2	148.2	189.8	202.8
Phenanthrene	8.3	42.3	159.9	156.4	181.6	184.2	204.2	204.2

These reagents in no wise react on the unsaturated acids of a fat. We must therefore attribute their accelerating power to their emulsifying action, which facilitates the hydrolysis of the fat globules in intimate contact with the water molecules.

Stress should be laid on this important fact, that no secondary reaction seems to intervene, the fatty acids obtained by this method being the unchanged hydrates of the acid radicals which were combined with the glycerol in the nonhydrolyzed fats.

It seemed to us that hydrochloric acid might serve to show even more clearly that the hydrolyzing action of water is simply accelerated by catalytic agents, the hydrochloric acid taking no part in the chemical reaction. Our experiments on this point are given in Table V:

Table V.—Hydrolysis of Oils and Fats with Hydrochloric Acid of Specific Gravity 1.16.

(100 grams of fat boiled with 100 cc. of acid.)

Oil or fat.	Original acid number.	After 24 hours.	Acid number of completely hydrolyzed fat.
Cotton	0.35	143.9	202
Whale	6.01	157.3	195
Colza	2.16	131.7	185
Lard	1.25	140.3	201
Tallow	11.15	150.0	200
Cocoa (copra)	18.75	204.9	260
Castor	1.22	49.14	190

A certain amount of hydrochloric acid having escaped in the gaseous state in these experiments, in the experiments given in Table VI a fresh addition of hydrochloric acid was made after taking each sample:

Table VI.—Hydrolysis of Oils and Fats with Hydrochloric Acid of Specific Gravity 1.16.

(100 grams of oil or fat and 100 cc. of acid; acid added after taking each sample.)

Oil or fat.	Original acid number.	Acid number after T hours.				
		$T = 2$.	7.	9.	12.	14.
Cotton	0.35	18.42	79.6	95.51	116.2	136.4
Whale	6.01	26.69	101.3	120.3	142.7	155.4
Colza	2.16	19.66	75.06	89.57	107.2	120.1
Lard	1.25	14.51	84.78	116.8	139.8	149.4
Tallow	11.15	43.39	112.5	131.7	153.2	167.0
Cocoa	18.75	79.73	184.2	210.5	221.4	230.8
Castor	1.22	44.4	47.3	49.0	51.4	51.4

Table VI—(Continued.)

	Acid number after *T* hours.					Acid number completely hydrolyzed fat.
	T = 16.	18.	20.	22.	24.	
Cotton	144.9	155.7	164.8	168.2	175.8	202
Whale	162.3	170.0	172.0	...	...	195
Colza	127.3	134.2	140.3	144.0	151.8	185
Lard	152.1	162.7	168.0	173.0	177.0	201
Tallow	173.3	178.9	183.3	185.2	186.8	200
Cocoa	233.4	239.8	241.1	246.1	250.1	260
Castor	47.9	49.2	46.8	44.4	41.64	190

In other experiments (published elsewhere) carried out for the purpose of accelerating still more, if possible, the catalytic action of hydrochloric acid, it was not found possible to obtain complete hydrolysis. In fact, the reaction slows up very much when the hydrolysis reaches 75 per cent. It is difficult to maintain, during the experiments, an intimate mixture of the fats and dilute acid; this might explain the slowing up of the reaction. By realizing a perfect mixture, such as an emulsion, it might be hoped to obtain complete hydrolysis, for the catalytic action of hydrochloric acid manifests itself, with time, even at ordinary temperature. Thus, cotton oil mixed with hydrochloric acid is hydrolyzed 75 per cent. after 213 days' contact.

We thus approach, step by step, the methods which Nature applies *in vivo*. The oleaginous seeds contain considerable quantities of fats, which have accumulated in them, to serve as nourishment for the embryo. How is this transformation brought about? It is certain that it begins by the hydrolysis of the fats, for Pelouze showed in 1855 that the seeds of the flax, the poppy, the camelina, the colza, peanuts, sweet and bitter almonds, contained a principle, then unknown, capable of effecting quite rapidly the hydrolysis of the oils in the seeds. Then the experiments of Müntz, in 1871, established the fact that the first phase in the utilization of the fats accumulated in the seeds takes place concurrently with the hydrolysis of the fats and that the observed acidity is due to the fatty acids liberated from the neutral glycerides.

This is a very important observation, which was, moreover, confirmed by Schützenberger in 1876. From that time date the attempts made to isolate the hydrolyzing principle. Maillot, in 1880, found in the castor bean a soluble ferment to which he attributed the lipolytic power. This fact was confirmed by Green and by Sigmund. Finally, thanks to the work of Connstein and his collaborators and to the ex-

tended investigations of Nicloux, these operations passed from the domain of the laboratory to that of industry.

Nicloux's cytoplasm, *i. e.*, the soluble ferment of his predecessors, behaves like a catalytic agent, obeying the physico-chemical laws which govern the speed of hydrolysis. Mixed with oil in the presence of water acidulated with a minimum quantity of a suitable acid or acid salt, cytoplasm effects the hydrolysis of fats *in vitro*.

It is the same phenomenon which is realized in cellular life during the germination of the oleaginous seed! Can we therefore put forward the view that all seeds containing fats in reserve for the nourishment of the embryo enclose at the same time an enzyme or cytoplasm or soluble ferment which, thanks to the water and carbonic acid always present in sufficient quantity to accelerate the progress of the reaction, hydrolyzes the fats at the moment of germination?

Might it not be the same in the animal organism? Might not the fats consumed for our alimentation be assimilated in a like manner? We know well the fundamental fact discovered by Claude Bernard in 1849 that the pancreatic juice collected through a fistula emulsifies fats; at the end of a short time the mixture contains free fatty acids. We know also that in 1854 Berthelot showed that the hydrolysis of mono-butyrin can be effected by the aid of the pancreatic juice. It seems to be hydrolysis, therefore, which represents the first phase in the assimilation of the fats! We have shown that lipase, a ferment contained in the liver, has an almost negligible hydrolyzing power, although it hydrolyzes ethyl butyrate rather easily; in fact, we were not able to hydrolyze *in vitro* more than 3 per cent. of fat. Our experiments have shown, on the contrary, that steapsin, a ferment contained in the pancreatic juice, has quite a large hydrolyzing power.

Steapsin, without doubt, effects the hydrolysis by emulsifying the fat, finely dividing the fat globules in such a way as to bring them into intimate contact with the water molecules which, in their turn, attack and split up the glycerides into diglycerides, monoglycerides, glycerol, and fatty acids. We thus come back to our fundamental point of view, *viz.*, that it is the water which effects the hydrolysis.

Inasmuch as in the laboratory potash or soda in alcohol (either ethyl or amyl) solution is used to accelerate the process of saponification, it might be thought that alcohol behaves like a catalytic agent. But if the least trace of water is rigorously excluded, the splitting up into glycerol and fatty acids

by means of alcohol is not effected.   If sodium ethylate, first recommended by Bouis, freed from all traces of water, is used as the saponifying agent, only the reaction indicated by the equation

$$(2) \quad C_3H_5\underset{\diagdown OR}{\overset{\diagup OR}{\rule[0.5ex]{1.5em}{0.4pt}OR}} + 3C_2H_5ONa = C_3H_5(ONa)_3 + 3C_2H_5OR$$
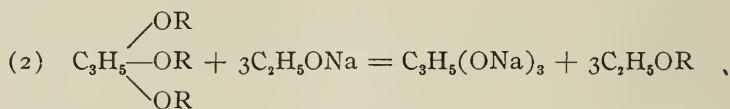
is realized.   Minimal traces of water are sufficient to decompose trisodium glycerate, first into disodium, then into monosodium glycerate, and finally into glycerol and caustic soda. It is the latter which, in its turn, hydrolyzes or, if you wish, saponifies the ethyl esters according to the equation

$$(3) \quad 3C_2H_5OR + 3NaOH = 3C_2H_5OH + 3NaOR.$$

It will be easily understood that in the laboratory operations where caustic potash and soda in alcoholic solution are used, the whole series of reactions enumerated above takes place, ending up in a first phase resulting from the successive reactions, the production of ethyl esters which, in their turn, in a second phase, are split up into glycerol and fatty acids, the latter, finally, being converted immediately into soaps by combining with the potash.   If the proportion of potash is less than that theoretically necessary for the formation of soaps, some ethyl esters and a quantity of soap corresponding to the amount of alkali used will be found in the products of the reaction.   Numerous experiments have confirmed this theoretical postulate.

The action of alkalies in alcoholic solution must not be considered as differing, theoretically, from hydrolysis in aqueous solution; the alcohol need only be considered as water, HOH, in which one hydrogen is replaced by a C_2H_5 or C_5H_{11} radical.   The reaction between the glyceride and alcohol may be represented by the equation

$$(4) \quad C_3H_5\underset{\diagdown OR}{\overset{\diagup OR}{\rule[0.5ex]{1.5em}{0.4pt}OR}} + 3C_2H_5O\text{—}H = C_3H_5\underset{\diagdown OH}{\overset{\diagup OH}{\rule[0.5ex]{1.5em}{0.4pt}OH}} + 3C_2H_5O\text{—}R,$$
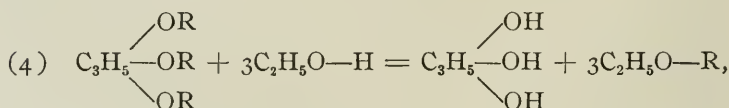
which sums up the three following equations:

$$(4a) \quad C_3H_5{\overset{\textstyle OR}{\underset{\textstyle OR}{\diagup}}}OR + C_2H_5O{-}H = C_3H_5{\overset{\textstyle OH}{\underset{\textstyle OR}{\diagup}}}OR + C_2H_5O{-}R;$$

$$(4b) \quad C_3H_5{\overset{\textstyle OH}{\underset{\textstyle OR}{\diagup}}}OR + C_2H_5O{-}H = C_3H_5{\overset{\textstyle OH}{\underset{\textstyle OR}{\diagup}}}OH + C_2H_5O{-}R;$$

$$(4c) \quad C_3H_5{\overset{\textstyle OH}{\underset{\textstyle OR}{\diagup}}}OH + C_2H_5O{-}H = C_3H_5{\overset{\textstyle OH}{\underset{\textstyle OH}{\diagup}}}OH + C_2H_5O{-}R.$$
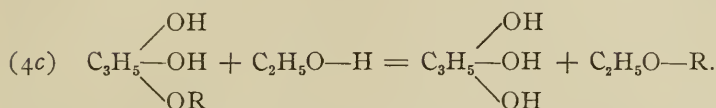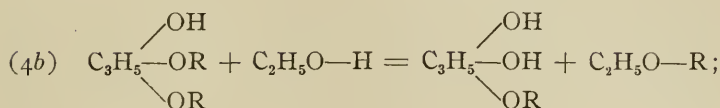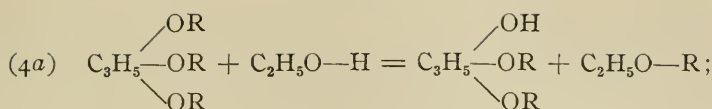
The final products would be glycerol and the ethyl esters of the fatty acids. The possibility of these reactions has not yet been demonstrated experimentally, but with anhydrous products and under high pressures, especially with the aid of a favorable catalytic agent, it is probable that the reaction would proceed largely according to equation (4).

It is thus that we expressed ourselves five years ago, but to-day our predictions have been confirmed by the alcoholysis effected by Haller. If a fat is heated with 2 parts of methyl, ethyl, or propyl alcohol, containing 1 or 2 per cent. of hydrochloric acid, until a homogeneous mixture is obtained, the neutral glyceric esters are transformed into methyl, ethyl, or propyl esters. Such is the methanolysis, ethanolysis, propanolysis of Haller, a beautiful method which will perhaps aid us in the future in analyzing, qualitatively, at least, the complex mixtures of glycerides contained in a natural oil or fat.

Let us go back and sum up again the mechanism of hydrolysis. It is the water alone which effects hydrolysis, and at a rather high temperature hydrolysis is effected in quite a short time. By adding to the water a catalytic agent, a base or strong acid, the temperature can be lowered and the time reduced. Finally, with a catalytic agent possessing a considerable emulsifying power, such as enzymes, hydrolysis can be effected at the temperature of the blood or even of the soil. This explains how the ferments of seeds or of the pancreatic juice favor the hydrolytic reactions of cellular life.

The same considerations, moreover, permit of a very simple explanation of the rancidity of fats. When rigorously protected from moisture, oils or fats maintain their neutrality

indefinitely. But if they are allowed to stand in contact with the organic matter from which they are extracted, such as the marc of fruits or the animal tissues, the casein of butter, etc., the hydrolysis of the glycerides increases rapidly and may attain considerable proportions. The formation of such a large quantity of fatty acids can be explained as being due to the action of water, favored by the enzymes which exist in considerable quantity and act as accelerators. Admitting that commercial oils and fats contain minimal quantities of ferments, the traces of water which they always retain suffice to effect the initial reaction, hydrolysis.

Such is the primary cause of the formation of fatty acids; such is the prelude, the initial phase, of rancidity. We know that commercial oils and fats contain free acids. Exposed to the action of atmospheric oxygen in the presence of light, the fatty acids undergo a certain modification and the fat acquires a disagreeable odor and a bitter taste. In such a fat the presence of volatile acids and perhaps of aldehydes can be proved; in other words, it has become rancid! We can, moreover, expect to find in rancid oils and fats di- and monoglycerides. Dierucin, which separates in a crystalline mass from rancid oil of colza, confirms in a striking manner this theoretical postulate.

We know that the cell itself effects the inverse reaction, *i. e.,* the synthesis of fats! In animals which consume fats in their alimentation, this synthesis is effected on a vast scale. We might be tempted to attribute this inverse reaction to the action of other enzymes. On the other hand, the opinion has been expressed that all enzyme processes can effect reverse reactions, hydrolysis as well as synthesis. Nevertheless we have not succeeded, in our experiments with steapsin *in vitro*, in producing the inverse reaction, *i. e.,* synthesis. But the number of experiments carried out is still too limited to permit of drawing general conclusions from them. Moreover, Pottevin, having previously shown that mono-olein is obtained synthetically from oleic acid and glycerol under the influence of pancreatic tissues, effected the synthesis of triolein by the action of pancreatic juice on the mono-olein in the presence of oleic acid. This synthesis was, besides, confirmed by Taylor, although this author did not succeed in preparing palmitin and stearin by the same method. But considering the enormous differences which must exist between syntheses *in vitro*, on the one hand, and *in vivo* on the other, these results are not entirely negative. It is nevertheless an

undoubted fact that in the organism there are rhythmical variations leading now to hydrolysis, now to synthesis, according to the local exigencies of the organs.

Let us not think, moreover, that we are already passing beyond the limits of the chemistry of the fats! The practitioner called upon to study the influence which the fat given in alimentation has on the composition of the butter of mammals could suggest no other explanations. We find, moreover, a perfect analogy, purely chemical, in the action of Twitchell's reagent. It was seen above that this reagent accelerates the hydrolysis of fats by water; if it is added to a mixture of fatty acids and glycerides and the water which is formed is eliminated, the fatty acids combine with the glycerol to form mono-, di-, and triglycerides, a reaction which is analogous to the synthesis of the glycerides, first effected by Berthelot. Platinum black can likewise act in a similar manner as an accelerator both of hydrolysis and of synthesis.

Do the synthetic methods for the preparation of the glycerides find an industrial application? The primary substances used in all the methods thus far elaborated being themselves the immediate products which the glycerides yield on hydrolysis, strictly speaking, these methods cannot be regarded as synthetic methods, since the point of departure is, in fact, the product which it is desired to obtain finally! This would no longer be the case if it were possible to prepare the fatty acids synthetically from different primary substances, such as the hydrocarbons found in abundance in natural petroleum. The problem of the synthesis of fats would then be really solved by converting a CH_3 group of the hydrocarbons boiling around 300° into a carboxyl group. Thanks to the method of *Grignard*, it has been possible to synthesize acids containing as high as ten atoms of carbon, and to prepare a di- and a trioctin by heating an octanoic acid with glycerol at 250°.

Will it be possible to prepare a stearin?

It must be remembered that the behavior in chemical reactions of acids high in carbon is essentially different from that of the lower acids.

Decidedly, Nature, silent and indefatigable, works in a manner less rough and, especially, more sure and efficacious than we do!

The biochemical synthesis of the fats is realized, in fact, on a large scale, in nature, by means of water and the simplest compounds of carbon, *viz.*, carbonic acid, aldehyde, etc. What are the consecutive phases which lead thus to the pro-

duction of a fat? As yet we do not know! It seems certain, nevertheless, that vegetable oils and fats originate from the hydrates of carbon.

It was Luca who first showed that mannite is transformed in the fruit of the olive tree into olive oil; Müntz likewise showed that glucose, saccharose, and starch undergo the same transformations in the seeds of the colza, the poppy, and flax.

But such processes do not enter into the domain of industrial application.

Natural oils and fats are, moreover, found in such abundance that their industrial preparation by synthetic methods is of no practical importance. Chemists ought rather to suggest to Dame Nature methods for the amelioration of the quality and for the increase of the quantity of the fats which she produces. Extended investigations must then be undertaken to determine the influence exerted by the seasons, the species of a plant, the climate, the soil, the breed, the nature of the alimentation, and even the idiosyncrasy of an animal, on the quantity and the qualitative composition of the fats. These qualitative variations, however small they may appear, are of the greatest importance for the industry. It is to the influence of the soil that must be attributed the difference in quality of the oils extracted from the Jaffa sesame, on the one hand, and from the Chinese sesame on the other. The same is true for olive oil from different sources! The investigations on oils now being carried out in Algeria and Tunis demonstrate strikingly the necessity of combining purely chemical researches with physiological, agronomic, and economic investigations in order to secure to the industry of the fats the coöperation of science.

As soon as the importance of the soil was recognized, the study of the proper methods to effect the amelioration of seed and fruit species, as the stock breeder has been doing for centuries, was begun. In the United States it was attempted to produce two varieties of maize seed, one containing a large proportion of oil, the other a small proportion. Here are some figures: Within the course of seven years it has been possible to produce a variety whose content of oil increased from 4.7 per cent. to 6.53 per cent.; inversely, another variety has been obtained whose content of oil has fallen from 4.7 to 2.97 per cent. By transplanting flax seeds rich in oil in soils where only seeds poor in oil are obtained, a decrease of the oil content is observed. American and Egyptian cotton seeds con-

tain about 23 per cent. of oil; when transplanted and cultivated in Bokhara they contain only 17.5 per cent.

What is the cause of this decrease? We do not know! It remains then for science to study these phenomena, still obscure at the present day, to choose and cultivate the species rich in oil; the farmer shall utilize these investigations and derive from them practical principles!

Meanwhile, the oil manufacturer is compelled to make these selections himself.

In fact, in order to manufacture edible oils, he selects the freshest and soundest fruits and seeds. Expressed cold, they give him almost immediately oils fit for consumption. Thus, for example, Jaffa sesames and Rufisque peanuts are the most highly esteemed for the production of table or margarin oils, while seeds from other sources furnish hardly any but ordinary edible oils or even oils for industrial purposes.

Thanks to its geographical situation and to its climate, France, and especially Marseilles, have played a most important rôle in the industry of oleaginous substances. It will be well then to sketch the history of its development in a brief historical review of the French and Marseilles oil industry.

The cultivation of the olive tree, introduced into France by the Phoenicians, gave birth to the industry of olive oil. It was formerly an agricultural industry, the precursor of the oil industry of our times. The fruits were triturated in a mill and the marc expressed by means of a screw press, analogous to the presses employed for grapes. The hydraulic press, conceived by Bramah in 1795, introduced a new source of force, easy to direct and of almost unlimited power. Bramah's invention brought about a complete revolution in the oil industry and it was not long before it attracted the attention of the Marseilles manufacturer. New seeds were introduced, the Marseilles press became widely distributed and its utilization was increased by the use of scourtins; the accumulator invented by Armstrong in 1843 was adopted. Thanks to the introduction of steel, a substance having an enormous resistance, the pressure, formerly limited by the resistance of the screw to rupture, was raised to 250–300 atmospheres. The press manufacturer's material permits of surpassing these pressures, but the use of the scourtins, of which the Marseilles people are so fond, prohibits it.

It was, moreover, not in one day that this degree of perfection was attained.

The first attempts to triturate flax seeds from the Levant date back to 1817. The same materials and the same method were used as in the manufacture of olive oil.

The north of France was competed against. There the wooden screw press was employed to express the seeds (native-grown) of the hemp, the mustard, the garden-poppy, the colza, and the flax; then it was replaced by the lever press and, shortly afterwards, by the wedge and cam press which had been used by the Chinese for centuries (and invented again in Holland in the 17th century). The cultivation of the colza, moreover, began to give way to that of the beet; the cultivation of the garden-poppy likewise decreased. The North had no more seeds to pour out upon Marseilles factories, the drain upon which increased with the daily augmenting population.

Marseilles, "the outlet of France on the Mediterranean," then turned towards the sea. The north of Africa possesses olive oil in abundance and it was already being exported as early as the 10th century. But this oil was generally prepared in the same manner in which the Dahomey negro prepares palm oil to-day, *i. e.*, by placing the fruits in a hole dug in the ground and waiting till fermentation of the mass makes the oil rise to the surface. African olive oil thus obtained, sharp, bitter, nauseating, could not suit the fine taste of the Frenchman, accustomed to the virgin oil of Provence. The oil industry did not yet exist south of the Mediterranean; there were not yet exported those large quantities of olive oils which are now brought to Marseilles for use in cutting the native oils.

The countries to the right and to the left of the Cannebière were then turned to and the sesames and poppies of Levant, the peanuts in the shell of the Cape Verde Islands and of Senegal were found. The oils of the first expression were easily sold as edible oils; the oils of the second and third expression found an outlet in the industries. The cake was given to cattle or returned to the soil as fertilizer for the early crops.

The native of Marseilles says that the Cannebière extends as far as India. It is not astonishing, therefore, that the sesames and poppies of India, the peanuts of Coromandel, the copras of Ceylon, and the mowrahs of India were brought to him. From the African coast arrived the palm oils and nuts! Finally there were imported seeds, the oils from which are

suitable only for the industries, the cottons of Egypt, the flaxes of Russia, and the colza of India.

The manufacture of seed oils became the monopoly of the large establishments of Marseilles and this city, with its 49 oileries and 1,557 presses, employing 3,726 laborers, working up daily 1,200 to 1,300 tons of seeds, reached its zenith in 1878. The oil industry extended as far as Bordeaux.

And the North, what was it doing while these rapid advances of the South succeeded each other? We have already mentioned that the colzas had given away to the beet. The oil of colza, for purposes of alimentation, had, moreover, been gradually rejected as the taste of the consumer grew more refined. The cultivation of the garden-poppy was of too small importance to be able to replace it. Alimentation requires solid fats, cow butter, lard, beef and even mutton tallow. But butter was a luxury for the purse of the workingman, and lard itself was dear, for at that time those immense importations from the United States of lard and its substitutes, artificial lards, mixtures of beef and cotton fats, containing but little or even no pork fat, were not yet known.

At this point the government stimulated inventive genius and started up a competition for the industrial production of a fat suitable for consumption, keeping well, and cheaper than cow butter. Mège-Mouriès put his process into practice in 1870 and the margarin industry became established in Paris, where it disposed of considerable quantities of beef tallows, furnished, with all the necessary properties and freshness, by the slaughter-houses of the metropolis. This new industry had first to overcome the popular prejudices which opposed its legitimate development. Neither the calumnies of detractors nor the machinations of the agrarians were able to prevent it from extending, almost triumphantly, into all the countries of the world, even into Australia, a country which is, *par excellence*, a producer of cow butter. Was it not, moreover, a real advantage to the working population, in the sense that it did away with the consumption of unwholesome fats from diseased animals and fats prepared under conditions of doubtful cleanliness? The progress of this industry could not be demonstrated more eloquently than by giving the statistics of production (Table VII):

*Table VII.—Production, Imports and Exports of Margarin, in
        Kilograms.*

County.	Estimated production.	Imports, 1906.	Exports, 1906.
Holland	75,000,000	56,210,100	53,890,800
Great Britain	50,000,000	55,479,100	805,700
United States	50,000,000	. . . .	. . . .
Germany	25,000,000	168,600	108,700
Denmark	26,000,000	8,710,000	360,000
France	25,000,000	65,663	6,366,930
Sweden	15,000,000	519,600	655,600
Norway	15,000,000	29,400	755,400
Austria-Hungary	15,000,000	792,400	1,406,200
Belgium	11,000,000	359	250,297

307,000,000

We may add that in the same year the exports of French
butter, fresh and salted, amounted to 19,760,000 kilograms,
the imports being only 5,172,000 kilograms.

By establishing the industry of edible animal fats, the North
began to dispute the leadership of the South in the field of
the fats. Marseilles, thus threatened, redoubled her efforts!
She too must manufacture solid fats for consumption. But
she turned to vegetable fats! The freshest copras were sub-
jected to treatment, processes of refining were invented, and
by going back to the known methods of Braconnot, Chevreul
and Dubrunfaut the oil was freed from its original odor and
taste. Vegetable butters appeared on the market! In
imitation of the processes of the stearin and margarin indus-
tries, the liquid parts, the olein, were extracted by pressure
from the solid oils, and the quite modern manufacture of
substitutes for cacao butter, known as "chocolate fats," was
established.

During the course of this contest for the supremacy in the
fat industry, the power of the Marseilles press began to be
doubted. In foreign countries the fat industry had acquired
gigantic dimensions, especially in England, the United States,
and also Germany. There had been installed the so-called
Anglo-American presses, then the powerful cage presses of
the most modern construction. These presses also made
their appearance in Marseilles, but whether the patriotism or
traditionalism of Marseilles was too strong, or the slow but
sure operation of the Marseilles press really was superior, no

great enthusiasm was ever manifested at Marseilles for this modern machinery.

Let us not forget, moreover, that the Chinese, with a primitive wedge press, by prolonging the pressure a whole night obtain a better yield than is secured with the most modern European presses.

Will these efforts to perfect her machinery, improve and develop her manufacture of edible oils, and create new, solid, alimentary fats, bring Marseilles to a new zenith greater than the first? In any case, at the present time Marseilles works up more than half of the oleaginous imports of France, greatly outdistancing her rivals, Bordeaux, Dunkirk, Havre, Dieppe, and Nantes.

Moreover, Marseilles does not limit herself to the expression of oleaginous fruits and seeds. Black olives, which cannot be used for feeding stock, contain too much oil to be rejected. So Marseilles has long since extracted them with carbon bisulphide, a method brought from England by Deiss and still utilized at present in the South. This process is extended to the treatment of damaged castor beans and sesame seeds and the nonalimentary oil cakes. Petroleum ether, employed on a large scale abroad, in England, Germany, and America, has not secured a foothold in the South; but it is not always on account of her conservatism, which, moreover, is legendary, that Marseilles opposes innovations! Quite recently, in fact, extraction by means of carbon tetrachloride, extolled as the ideal of all solvents on account of its noninflammability, has been tried industrially. But the practical manufacturer soon found that the advantages so much preached were rather illusory than real. The cost of the solvent is too high, and the machinery, whose resistance to the attack of the hydrochloric acid liberated by the solvent in the presence of traces of moisture is more than doubtful, is itself too expensive, and so the use of carbon tetrachloride has already been abandoned.

France imports, on an average, 800,000 tons of oleaginous substances, valued at about 270,000,000 francs, and exports about 50,000 tons, valued at 38,000,000 francs. Deducting the fruits of the olive tree, French soil produces less than a tenth of this amount. The production of oil from native fruits and seeds, including olive oil, amounts to about 150,000 tons, of which 15,000 to 16,000 tons are olive oil. France imports 115,000 tons of different oils and fats and exports

50,000 tons, so that the consumption amounts to about 120,-
000 tons.

The English industry of oleaginous products, nevertheless,
surpasses by far that of France. Germany already imports
nearly 1,000,000 tons of oleaginous substances, but exports
about 300,000 tons. Nevertheless, the native production of
flax and colza is not negligible.

Why is Marseilles, formerly the great metropolis of fats,
losing its monopoly? Why do those ships laden with cotton
from Egypt and Bombay, colza from India, sesame from the
Levant, India, and China, palm nuts from Africa, pass by
Marseilles and Bordeaux, carrying with the oleaginous prod-
ucts the real industries of Marseilles?

Those are questions which touch upon political economy.
It is not for us to discuss them, therefore, especially at this
time when it is proposed to place an import tax on oleaginous
products.

Moreover, it should be pointed out that the cultivation of
oleaginous seeds is decreasing in Europe and that the culti-
vation of wheat and the beet is more and more gaining the
ascendancy. Except in the cultivation of the olive tree,
which requires the warm climate of southern Europe, Russia
alone still plays in Europe an important rôle as a producer of
oleaginous products.

The United States and South America have become formid-
able competitors of the flax and cotton seed producers of the
old world, but it is especially as purveyor of maize and animal
oils and fats for the old world that the new world means to
establish itself! Brazil itself is ready to put on the market
its considerable wealth of solid vegetable fats.

Does the old world therefore run the risk of being sup-
pressed? We do not think so. The production of oleaginous
substances in the warm countries—tropical and western Africa,
India, Indo-China—can be indefinitely increased. The colo-
nial exposition of Marseilles gave us a vivid illustration of the
sources of oleaginous products which are awaiting exploita-
tion through the development of the means of communica-
tion by land and sea. China herself seems to be awakening
from her slumber; she exports peanuts, sesames, vegetable
tallow, in quantities which yearly increase. At this very
moment she is sending us Soja beans, the oil from which bids
fair to become a competitor of cotton and maize oil.

Such are the raw materials in the industry of the fats! A
considerable quantity, which moreover is increasing from

day to day, finds use in the industry of edible oils and fats, but the greater part is employed in the great industry of the fats, the stearin and soap trades.

The processes of the stearin industry are well known; the candles exhibited in successive expositions by French houses have shown to the whole world the importance and the degree of perfection attained by this industry, one of the monuments of French chemical industry. Gas and electricity keenly compete with it, but the production does not suffer much therefrom. For gas are required a large establishment, long piping, cocks, matches. For electricity boilers, motors, electric wires, special lamps, are necessary. And then the consumer is not protected from a possible strike. As to the candle, it is carried in the pocket. The candle and a match, there is the whole installation. It is the ever-ready light! It ought to have been invented if it had not already existed.

The stearin industry no longer witnesses those great inventions, the admirable succession of which marked an epoch in its history; the great efforts of the first half of the last century seem to have exhausted its sources. It is only these details, those difficulties in the recovery of materials, those little economies of raw substance and labor which make the success of a factory and make the greatest demand, perhaps on the perseverance and ingenuity of the practitioner. New materials are therefore sought, palm oils, mowrahs, Illipés, vegetable tallows, bone tallows, regenerated fats, etc. The advantages offered individually by saponification with lime under pressure, on the one hand, and with sulphuric acid on the other, the one giving a greater yield of glycerol of better quality, the other a greater quantity of solid acids, are combined. It is the "mixed process" of the modern stearin industry. Saponification by means of Twitchell's reagent, representing another kind of "mixed process," has already been mentioned above. The fats are hydrolyzed with this reagent, the product of hydrolysis acidified with concentrated sulphuric acid, in order to transform the oleic acid into solid products, and the mass distilled in the usual way. The presence of a considerable quantity of free fatty acids being one of the essential conditions in this process it is especially adapted to the utilization of inferior fats. The large slaughter houses of Chicago supply considerable quantities of these. This is why this process has extended to several establishments in the United States. Nevertheless, a number of disadvantages are attached to it, and it has not been able to pene-

trate into and maintain itself in any European stearin factory.

Another innovation! In the attempt to do away with the pressing out (hot or in the cold) of the fatty acids, it was discovered that a dilute solution of sulphostearic acid dissolves oleic acid alone, the solid fatty acids remaining undissolved in this medium. We have seen this process applied industrially in the factory of the inventor at Turin.

A new rival of stearic acid appears in mineral waxes. The French stearin industry, always proud of its reputation, has thus far refused to use those American and Scotch paraffines which are used abroad in enormous quantities. The French consumer demands a beautiful, hard, brittle candle of high melting point. But now that paraffines from Rangoon and Assam are obtained which melt higher than stearin itself, it will not be long before the lure of low cost will attract to them the attention of the French stearin manufacturer.

A great problem of the stearin industry still remained to be solved, *viz.*, the complete transformation of oleic acid into stearic acid. Just like stearic acid, oleic acid contains 18 atoms of carbon and 2 atoms of oxygen, but differs from it by having two atoms of hydrogen less. One of the easiest processes in the domain of organic chemistry to carry out is hydrogenation by means of sodium amalgam. Nothing simpler than to treat the oleic acid with this reducing agent in order to convert it into stearic acid, a substance which is ideal for the stearin industry! But oleic acid rebelliously refuses to take up hydrogen under these conditions. The same is true of its mono- and dibrom derivatives, an indirect method which it seemed to us useful to try.

Saponification with sulphuric acid pointed out the way which it seemed should lead to the conversion of oleic acid into solid substances, and for the last fifty years this reaction has been thoroughly studied. But reversible reactions intervene, and large quantities of oily products which cannot be utilized are formed.

It was attempted to prepare palmitic acid, a substance well adapted to the needs of the stearin manufacturer, by fusing oleic acid with caustic alkalies, and Olivier and Radison installed such a plant in the stearin factory of Fournier, at Marseilles; but the candles so obtained, which were exhibited at the exposition in 1878, have a rancid odor and feel greasy, and this process has been abandoned.

Hydrogenation by means of electric discharges in an atmosphere of hydrogen was then thought of.

With the classic work of Sabatier and Senderens as guiding thought, it was later proposed to use metallic cathodes of palladium, platinum, and nickel, covered with a spongy layer of the same metals, in an alcoholic solution of oleic acid. But it is not such methods which will lead to the goal! It is rather the method of Sabatier and Senderens which marks a new era in the history of the solution of this problem.

Very shortly after the publication of the first monumental researches of these scientists on the hydrogenation of organic bodies in the presence of finely divided nickel, a German plant took out a patent for the conversion of unsaturated fatty acids or their glycerides into solid substances. Having already carried out laboratory experiments based on the principle of the method of Sabatier and Senderens, we repeated the experiments described in the patent, but were unable to obtain marked reduction. The product cakes together and contains nickel oleate. As far as we are aware, moreover, this process has never entered into the domain of practical industry.

Taking up again our study of the reaction of Sabatier and Senderens, we succeeded in obtaining a quantitative yield of stearic acid. Our first lack of success was probably due, then, to the fact that our contact substance had become inactive. We would say in the modern language of chemistry that the nickel was "poisoned." Almost simultaneously, Bedford and Williams took out a patent for the reduction of organic substances by the Sabatier-Senderens method; Schwoerer likewise had patented an apparatus for the transformation of oleic into stearic acid by the contact process. Finally, Sabatier himself has taken out a patent on this subject.

But this is not yet the final word. Paal and Roth recommend a hydrosol of palladium as a catalytic agent and carry out the hydrogenation at ordinary temperature. Olive, castor, and cod liver oils are converted almost completely into solid saturated fats. Oleic acid is thus reduced, in large part, to stearic acid. Here is enough, then, for the near future for the stearin manufacturer.

No one is ignorant of the considerable development which the soap industry has undergone during the last few years, and it is known that there are immense establishments where household soap is produced daily by the hundreds of tons.

It is not "augmented" or "charged" soaps which are manufactured and sold in such large quantities. They are soaps of

a degree of purity such as the imagination of the soapmaker of the first half of the last century could not have conceived, soaps free from caustic alkali and practically free from carbonate of soda. They are soaps containing from 63 to 64 per cent. of fatty acids—the maximum amount which a boiled soap can contain—and 29 to 30 per cent. of water.

In a word, it is the purity of household soap which characterizes the soap industry of to-day. The consumer becomes more and more exacting, demands not only a pure soap, but one of a firm consistency, not too hard, and of an agreeable color. The thrifty housewife who used to lay away her soap to dry above the stove or hearth to remove the excess of water has well-nigh disappeared. Time is money! Those excessively hard soaps made of olive oil or beef tallow, sole assets of the soapmaker of bygone days, are no longer wanted!

The mottled soap of Marseilles, that soap of legendary repute, contains only 58 to 59 per cent. of fatty acids; its water content is as high as 35 per cent.; moreover, it contains a few per cent. of mineral salts. It is therefore no longer a pure soap according to the definition given above. That is why its consumption and manufacture, formerly considerable, are gradually decreasing, even in the South, its native soil.

The mottled soap of Marseilles, the product of the slow evolution of that happy symbiosis of olive oil and saliferous plants, suffered its first serious modification as a consequence of the brilliant discovery of Leblanc. The soap resulting from boiling olive oil with the lyes obtained with artificial soda was harder than its predecessor, and the olive oil was mixed with walnut and poppy oils. Curious thing, such an addition was then considered as fraudulent! But the ordinary oils of sesame, peanuts, palm nuts, and cocoanuts, which needed an outlet, forced themselves in increasing quantity on the attention of the soapmaker. They began to be employed and even to be substituted completely for olive oil, and it is thus that the manufacture of pure, uniformly colored soap, which will before long give the death blow to mottled soap, arose.

The intelligence of the soapmaker is manifested in his skill in mixing the raw materials placed at his disposal in such a way as to obtain a soap exactly adapted to the desired purpose. In that consists the art of the soapmaker of our day.

That is why, while still using the open pan method of work, he studies experimentally the individual properties of the raw materials in order to derive from them practical formulas. In this connection we recall with satisfaction the work of

Merklen. Let us hope that it will stimulate the scientific activity of the French soap factories!

The saponification of neutral fats in the open pan is the natural process of the soapmaker. It is the one which gives us products of the best quality, beautiful color and suitable hardness. It gives us at the same time saponification lyes which contain almost all of the glycerol of the neutral fats, the extraction of which offers no difficulty, providing the alkaline lyes used are pure, a condition easily obtained at the present time. The modern soapmaker no longer pours his exhausted lyes into the river or sea, he keeps them and treats them scientifically to recover the "crude glycerol of the lyes," which, thanks to the invention of Sobrero, pupil of Pelouze, is so easily disposed of in the markets of the world.

The profits which the recovery of the glycerol brought to the large soap factories of France, England and the United States soon attracted the attention of the countries where the manufacture of soaps was still in that intermediate state of evolution of an industry trying to rise from the condition of a small trade, *quasi* domestic, to that of a great chemical industry. New methods were sought and, going back to the known processes, the manufacture of soaps from oleic acid, a sister industry to the stearic industry, was imitated. It was attempted to introduce into the soap factories the autoclave, thanks to which would be obtained the glycerol from the saponification, and fatty acids yielding soaps by simply neutralizing with carbonate of soda! The small soapmaker, mistrusting claims as persistent as they were insistent, at first refused to adopt machinery of which he knew only the dangers of explosion. That is why we saw arising those "deglycerinating" establishments where the glycerol is extracted by means of the autoclave. The fatty material was offered to the small soapmaker as raw material, as an inducement for the adoption of a process which was more economical and gave a better yield. But the soap is of an inferior color and consistency! It was attempted to remedy these serious defects and the pressure in the autoclave was diminished to five or six atmospheres and zinc oxide and powder were used. In this way the hydrolysis is reduced to about 80 per cent. and the yield of glycerol is decreased, while it is impossible to obtain a soap which can compete in quality with the product of the open pan process. Moreover, the costs of manufacture are not lower than with the latter process.

Decidedly, it was not the ideal process for the manufacture

of soap! Truly, soap could not be lowered to the level of a by-product, and in the end the great soap factories of the world did not adopt this method. We have even seen in several soap factories the machinery for heating in the autoclave idle, industrial experience having shown that the principal product, soap, was of a quality distinctly inferior.

Before long there appeared two rival methods for deglycerinating fats, both of which furnished a crude product still containing 15–20 per cent. of neutral glycerides. Great claims were also made for them, a thing which truly seems inseparable from everything connected with the soap industry! These were fermentative hydrolysis and the Twitchell process, the latter originating from the stearin industry and adapted to the exigencies of soap manufacture.

The criticism made above is also applicable to these two processes. Although yielding a product of better color than the autoclave process, fermentative hydrolysis involves considerable losses of fat; moreover, the raw material to be hydrolyzed must not melt higher than 35° nor contain any considerable quantity of free fatty acids. The Twitchell process, on the other hand, is better adapted to raw materials rich in free fatty acids. It is the process to be preferred for short tallows, waste fats; but it goes without saying that soaps made thus are also darker.

But the pursuit of glycerol did not yet stop here. Going back to the beginning of the stearin industry, the saponification with lime in open vessels was revived with this modification (which, to be sure, is useful) that the heating was not continued till the lime soap became hard and brittle. Some small soapmakers adopted this process especially for nauseous bone fats, which the lime deodorizes, while, at the same time, saponifying them. But the glycerol obtained is easily susceptible to fermentation, the operations are long, wearisome, the losses considerable, absorbing the profits which the recovery of the glycerol would bring.

We do not believe that there is any future for the deglycerinating processes. It is still the open pan process which will carry off the palm to-morrow, as it has done yesterday. Let the price of glycerol go down and these processes, whose existence is already ephemeral, will cease to be applied!

But happily for the soap industry, the lowering of the price of glycerol is still far off. That is why the small factories themselves are hastening to adopt the most perfect machinery

for the evaporation of the liquors of the soap industry, *i. e.*, for the evaporation in a vacuum.

The crude glycerol of the lyes of the soap factories is to-day obtained in such a state of purity that the greater portion of dynamite glycerols are obtained from this source. Nineteen years ago we prepared, on a large scale, the first chemically pure glycerol by starting from the crude glycerol of the lyes. Since then many establishments prepare chemically pure glycerol in the same way.

The quantities of glycerol extracted from the lyes of soap factories are rapidly increasing. A personal estimation leads me to evaluate the production of glycerols in France at 15,000 to 16,000 tons a year, *i. e.*, 7,500 to 8,000 tons of saponification glycerols of 28° Bé. (of which 2,000 tons are obtained from soap factories which use the deglycerination process, and 4,5000 to 5,000 tons from the stearin industry), and 7,500 to 8,000 tons of crude glycerols from the lyes of soap factories. We estimate that Great Britain produces about 25,000 tons a year and the United States 13,000 tons. For the other countries we have been unable to obtain authentic data.

A by-product which yesterday was cumbersome, even embarrassing, glycerol is to-day the plank which saves the soap factories. It is the recovery of the glycerol which binds the soap industry to the great chemical industries of modern explosives!

The industry of the fats is based on solid foundations. Nature gives us the raw materials in unlimited, inexhaustible quantities; science teaches us the methods for transforming them into useful derivatives of greater value; the manufacturer applies these methods to the raw materials to increase the well-being and the comfort of the human race.

Now, as in the past, the stearin and soap industries hold an honorable rank in the hierarchy of industrial chemistry! And yet these industries seem to us but to barely touch on the confines of the industrial domain of the fats. It is but the first stage in the victorious march of the industry of the fats! The chemistry and industry of boiled oils, the chemistry and industry of oxidized and ozonized oils, of vulcanized, iodated, brominated, chlorinated, sulphonated, nitrated oils, the industry of soaps with metallic bases, and a multitude of others, but await the coming of ingenious inventors.

And just as the first application of chemical analysis to the fats led, with so much success, to the creation of the stearin

industry, likewise the future progress of the industries of fatty substances will depend on the development of the chemical analysis of fats.

Lost in the darkness of the development of the soap industry, analysis first appears in the 18th century. Geoffroy, Junior, and Maquer published some analyses of soap. They determined the quantity of water by evaporation; they separated the fatty substance, still considered as the original fat, by means of hydrochloric acid and weighed it. These are the methods still employed to-day to determine the content of water and insoluble fatty acids. They determined also the quantity of alkali, weighed as sodium chloride or carbonate. Chevreul, employing analysis with an extraordinary skill and ingenuity, discovered stearic, margaric, oleic, and the volatile butyric, caproic and capric acids; he gave also very clear indications as to the existence of a phocenic and a hircic acid. The method of separating the volatile and insoluble fatty acids, a problem which even at the present is not yet solved in a perfectly satisfactory manner, was thus brought out. Then Chevreul attacked the problem of the separation of oleic from the saturated acids and solved it in a way which is truly surprising.

Three great groups of fatty acids—volatile, insoluble, unsaturated—were clearly distinguished, were established. It remained to fill some gaps. Boudet, while studying Poutet's reaction, found elaidic acid; Fremy isolated palmitic acid (a discovery which is important in the sense that it contributed to elucidating the nature of margaric acid); Bussy and Lecanu added a new class of fatty acids, that of ricinoleic acid. The work of the French school drew attention abroad; myristic, lauric, behenic, archidic, erucic, hypogeic acids were isolated.

But these were only the first foundations, however solid they might be, laid down whereon to build the edifice of the analysis of the fats. The practitioner, forced to get his bearings in the midst of the disconcerting multiplicity of the fats, had need of clear, even rapid, methods for discovering the adulterations which unscrupulous manufacturers and merchants imposed on commerce with that impunity which borrows its strength from the powerlessness of the chemist. He then had recourse to the determination of the specific gravity, of the melting and freezing points, and of a few other physical properties, to the test for elaidin, and especially to those

color reactions which still have too much attraction for a number of chemists, especially in France.

It was not yet clearly seen, as we showed 15 years ago, that all color reactions are due to foreign, adventitious substances, dissolved in the oils and fats. Most of these substances, supposed to be characteristic, have now disappeared from the commercial products, and there remain but the reaction of Baudoin for sesame oil and that of Halphen for cotton oil. Even these, considered thus far as precious reactions in qualitative analysis, are beginning to lose some of their importance.

It was especially owing to the lack of better methods that these color reactions flourished. Quantitative methods were needed!

Cailletet first proposed, in 1857, to determine the quantity of bromine absorbed by various oils and fats. It is the prototype of that modern method of the iodine number, a method of the most precious generality and reach for the identification of oils and fats, indicating in a certain manner the class or group to which belongs each natural oil and fat. The elaboration of the quantitative methods pointed out by Chevreul was continued. Oleic was separated from palmitic and stearic acids, the soluble from the insoluble acids.

Going back to the method applied by Chevreul, the quantity of alcoholic potash necessary to effect the complete saponification of each oil and fat was determined, and this determination was made by the volumetric method recommended by Gay-Lussac.

There were then found those important numbers which make it possible to differentiate in a manner as rapid as it is exact cow butter and cocoa oil on the one hand and colza oils on the other from most of the ordinary oils and fats. The iodine number, the saponification number and Reichert's number became the ordinary tools of the expert chemist charged to discover the adulterations of foodstuffs.

It was especially the adulteration of edible fats and oils, of butter, lard, olive oil, which had constrained the public analyst to elaborate these so-called quantitative methods. And the analyst was master, even if but temporarily.

Adulterations becoming more complex and more and more subtle, new methods, of a greater degree of perfection, to conquer the adulterator, had to be devised. Thorough study of the work of Chevreul led to methods based on the difference of solubility; Maumené studied and applied the thermic test

with sulphuric acid; Amagat and Jean introduced the oleo-refractometer.

But the adulterator kept pace with the progress of analysis and he soon adapted himself, with an extraordinary skill, alas, to the methods employed by the public analyst. With an ingenuity worthy of a better cause, the adulterator takes advantage of all those variations and anomalies which Nature presents in the oils and fats which she furnishes us.

It was therefore necessary to start again, and again the work of Chevreul was gone back to!

But do the known fatty acids exhaust all the possibilities, all the variations of which Nature may be capable? No! A thorough study of the drying oils showed the existence of linolenic and of linoleic acids, representatives of two new series of fatty acids; Arnaud's tariric acid is related to linoleic acid. Juillard found a dihydroxyl acid in castor oil, and even natural bibasic acids were discovered. But it is not only open-chain fatty acids which Nature uses for the synthesis of fats! For now there were discovered cyclic acids having rotatory power, the chaulmo-ogric and hydnocarpic acids extracted from chaulmo-ogra fats and their congeners by the happy hand of Power.

Stearic acid, a saturated acid with 18 carbon atoms, contains 36 hydrogen atoms; oleic acid contains two atoms less, and it absorbs two atoms of bromine or iodine.

Linoleic acid contains four atoms of hydrogen less and absorbs four atoms of bromine or iodine. Chaulmo-ogric acid, isomeric with linoleic acid, absorbs only two atoms of iodine, but as we have already pointed out, it contains a cyclic grouping. Linolenic acid contains six atoms of hydrogen less than stearic acid and absorbs six atoms of bromine or iodine. All these unsaturated acids can be converted into stearic acid by the method of Sabatier and Senderens.

Is linolenic acid the least saturated of the natural acids containing 18 atoms of carbon which are found in natural fats? Fish oils absorbing about the same quantity of iodine as the drying oils often attracted the attention of analysts. But it is only quite recently that a thorough examination disclosed in the oils of marine animals the existence of a new acid in considerable quantity. It is clupanonoic acid, containing 18 atoms of carbon and 28 atoms of hydrogen; it absorbs eight atoms of bromine or iodine. There is no doubt

that this acid can be transformed into stearic acid by suitable treatment.

On the other hand, a thorough study was begun of those foreign substances, the oils and fats comprised under the name of unsaponifiable substances. Among them was discovered cholesterin, an important member of the group of adipoceres, already studied by Chevreul. The great master had already recognized its alcoholic nature. Phytosterin, "the cholesterin of plants," was also found.

The investigations of Bömer, as painstaking as they were important, showed clearly that all oils and fats of vegetable origin are characterized by the presence of phytosterin (now called sitosterin), and all oils and fats of animal origin by the presence of cholesterin.

Here is a difference of great importance! It is chemical analysis apparently introducing us into the mysteries of the laboratory of Nature, disclosing the system by which she works. The tests for the acetate of phytosteryl, based on these investigations, gives us a means of classifying oils and fats according to their origin as vegetable or animal oils. That is not all! It allows us to discover minimal quantities of vegetable oils and fats added fraudulently to oils and fats of animal origin. Minimal quantities of cocoa oil in cow butter, or a few per cent. of cotton oil in lard, can be disclosed with absolute clearness.

Yet a little while and we shall be able to solve the inverse problem, the detection of small quantities of animal oils and fats in vegetable oils and fats. Olive oil will then no longer be adulterated with lard oil!

The test for the acetate of phytosteryl and the iodine number are, in a word, the two great principles, based on analysis, which we have adopted to establish a classification of the natural glycerides. We propose a natural division into fats of vegetable and of animal origin, and a subdivision into liquid fats, or oils, and solid fats of vegetable and animal origin. *Natura non facit saltum*; so too, we cannot expect a very sharp division.

The main features of analysis sketched in our rapid review lead then to more detailed subdivisions.

Here are these divisions brought together into a synoptic table:

Table IX.—Fats.

I. *Oils and Fats of Vegetable Origin.*	II. *Oils and Fats of Animal Origin.*
A. Vegetable oils.	A. Animal oils.
1. Drying oils.	1. Oils of marine animals.
2. Semidrying oils.	*a.* Fish oils.
a. Cotton oil group.	*b.* Liver oil.
b. Colza oil group.	*c.* Blubber oils.
3. Nondrying oils.	2. Oils of land animals.
a. Almond oil group.	*a.* Semidrying oils.
b. Olive oil group.	*b.* Nondrying oils.
c. Castor oil group.	
B. Vegetable fats.	B. Animal fats.
1. Chaulmo-ogra oil group.	1. Drying fats.
2. Laurel oil group.	2. Semidrying fats.
3. Palm oil group.	3. Nondrying fats.
4. Nutmeg butter group.	*a.* Body fats.
5. Cacao butter group.	*b.* Milk fats.
6. Cocoa oil group.	
7. Dika butter group.	

Drying oils of vegetable origin are characterized by their content of linolenic acid; semidrying oils by the presence of linoleic acid. The two groups of cotton and colza oils are differentiated by their saponification numbers, the presence of erucic acid in colza oils producing a considerable lowering of this number.

The class of nondrying oils, with the exception of the castor oil group, which contains considerable quantities of ricinoleic and other hydroxylated acids, is characterized by the preponderance of oleic acid. The almond oil group still contains small quantities of linoleic acid. Peanut oil, which belongs in the olive oil group, contains arachidic acid, which is determined by Renard's method.

Among the vegetable oils, the polarimeter distinguishes the chaulmo-ogra group.

The members of the laurel oil group still contain considerable quantities of oleic acid.

With palmitic acid predominating, we come to the palm oil group; with myristic acid, we have the nutmeg butter group. When the proportion of oleic acid decreases considerably and that of stearic acid begins to become more pro-

nounced, we reach the representatives of the cacao butter group.

Oils containing volatile acids in considerable quantity constitute the group of cocoa oil. The same oils are characterized by considerable quantities of lauric acid. When the volatile acids disappear while lauric acid still preponderates, we reach the dika butter group.

Let us consider in the same way the oils and fats of animal origin. The oils of marine animals are characterized by clupanonoic acid, those of land animals by oleic acid. The drying and semidrying fats of animal origin contain acids less saturated than oleic acid, perhaps isomers of linolenic and linoleic acids, if not clupanonoic acid itself, which seems probable, at least for the fat of the polar bear.

The nondrying animal fats are divided into two groups, the body fats and the milk fats, both being clearly differentiated by the absence or presence of volatile acids. Milk fats are the perfect analogues of the cocoa oils!

By adopting this point of view, the table above shows us what path analysis must in the future follow, combining its methods with purely scientific investigations in order to make new conquests. This alliance, while helping industry, will also furnish the public analyst, who is all at sea and is already appealing to the law for aid, with the indispensable weapons for the bitter and ever renewed warfare which he is waging with adulterators.

For a time it seemed that analysis did not find support in the fertile soil of Chevreul's native country. But for some time now efforts in this direction have been redoubled. Müntz and Coudon are showing the analyst how to detect small quantities of cocoa oil in cow butter; Haller is beginning to penetrate more deeply into the composition of natural fats; others follow him.

The ideal of a complete analysis of the fats is to effect the isolation and identification of all the acids of which it is composed, just as the elements of a mineral are isolated and identified. A task which cannot be realized to-day; it will be the problem of to-morrow!

It is almost a century since Chevreul made that memorable analysis of a soap which laid the foundations on which has arisen the modern edifice of the fats through which we have just passed. May another Chevreul rise in this midst, where the genius of the master has not ceased to inspire brilliant successors.

Let us cultivate analysis! It will fructify the chemistry as well as the industry of the fats! J. LEWKOWITSCH.

THE PREPARATION OF ALCOHOL AND ARTIFICIAL SILK FROM CELLULOSE.

Several recent articles, one on the preparation of alcohol[1] from sawdust and other wood waste, and the others on the preparation of artificial silk[2] from cellulose, both in the form of cotton and wood, are of special interest at this time when the question of the conservation of the natural resources and the utilization of waste materials is regarded as of fundamental importance for the present and future welfare of the race. Any method which will enable us to make use of waste products will be of great value, and although at the present time much of the artificial silk is made from cotton, waste cellulose materials are being used, to some extent, in its production, as in that of alcohol. Practically all of the commercial alcohol is prepared by the fermentation of sugars obtained by the hydrolysis of starch or from fruits or the noncrystallizable by-products of sugar works. At the present price of corn, about $25.00 per ton, as one ton of corn produces about 90 gallons of 94 per cent. alcohol, the cost is about 28 cents per gallon for raw material alone. For alcohol made from molasses it is about 22 cents, and for that from potatoes about 21 cents. By the use of sawdust and other wood materials the cost of the raw materials can be reduced to 2 to 2.5 cents per gallon, the price depending upon the transportation and handling necessary. About ten years ago a method was devised by Dr. A. Classen for converting the cellulose of these waste materials partly into fermentable sugar by the action of sulphur dioxide and steam under pressure. While the process worked successfully on an experimental basis certain defects developed when it was used on a commercial basis which rendered it unprofitable.

This lack of success was due (*a*) to the fact that it required from four to six hours to digest one and a half to two tons of material; (*b*) to the formation of large amounts of sulphuric acid which caused the production of gums and caramel and made the extraction of the sugar a long and expensive process; and (*c*) to the delay and expense due to the injury of the lead lining of the converter. Since the use of this process

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[1] R. F. Ruttan: J. Soc. Chem. Ind., **28**, 1290 (1909).

[2] W. P. Dreaper: *Ibid.*, **28**, 1297 (1909). A. Colin: Rev. Gén. Chimie, **12**, 40 (1909).

was abandoned engineers and chemists have been conducting experiments and have succeeded in overcoming the difficulties mentioned above, thus making the process thoroughly practical. By reducing the time of digestion to forty-five minutes they have reduced the amount of sulphuric acid and gums formed, and by lining the digester with fire-brick have increased the life of the apparatus. The digester now used is of steel with the fire-brick lining set in a cement of lead oxide and glycerol and measures 12 by 8 feet. The sulphur dioxide and steam are introduced through a perforated pipe which passes through the trunnions of the cylinder. After the digestion is complete the material is extracted and the solution is fermented and distilled, some malt being added to furnish food for the yeast. The alcohol obtained is clear, has no odor nor flavor of wood, contains no methyl alcohol nor fusel oil, but does contain slight traces of furfurol and aldehyde. Thus far no efforts have been made to reclaim the turpentine and acetic acid which are also extracted; but this problem will no doubt receive attention at the proper time. At present the residue left after the extraction is pressed into cakes, partly dried and used as fuel.

The author estimates that a plant with a capacity of 200 tons of sawdust per day can produce alcohol at a net cost of 10.8 cents per gallon, while the Alcohol Co. claim that they can produce it for 7 cents. Denatured alcohol costs the consumer 45 to 60 cents, while it should not cost him more than 20 to 25 cents.

It is generally assumed that the formation of sugars is due to the hydrolysis of the cellulose element of the wood. A number of chemists have pointed out that the average composition of wood, with the exception of several hard woods, is:

	Per cent.
Cellulose and oxycellulose material	65
Noncellulose material	35

In the production of alcohol by this method about 35 per cent. of the material, corresponding to the amount of noncellulose material present, is converted into sugar, while the residue of cellulose, amounting to 65 per cent. of the original material, does not yield sugar even when treated again in the same way, nor does a true fibrous cellulose (absorbent cotton) show any action when treated in a similar manner. It would therefore appear that, under the conditions of these

experiments, the true cellulose and the oxycellulose are not seriously altered chemically, while the lignone complex is capable of yielding sugar.

Should this prove to be the case, it might be possible to obtain alcohol from wood pulp and then use the residue (65 per cent. of the original) for the preparation of paper.

While the production of artificial silk has been suggested by several persons, the real birth of this industry was due to Count de Chardonnet, who, with the results described in a sealed document, deposited with the Academy of Sciences of Paris in 1884 and opened in 1887, as a basis, had so developed his method as to win a Grand Prix at the Paris Exposition of 1889. From that time the work has gone on steadily but slowly, as enormous difficulties had to be overcome before the industry could be placed on a paying basis. Many of the details of the methods are necessarily secret, as they could not be protected by patent.

One of the difficult problems, which has, however, been solved within the past year, was the recovery of the alcohol and ether from the wash liquors. As several liters of alcohol are used in the production of each kilogram of silk, the recovery of the solvents becomes a matter of the greatest importance.

Three methods for the preparation of artificial silk are in use at the present time on the large scale, *viz.*, the nitrocellulose, the cuprammonium and the viscose methods. In the first method, the nitrocellulose is dissolved in alcohol and ether; in the second the cellulose is dissolved in an ammoniacal copper solution; and, in the third, the mercerized cellulose is dissolved in carbon disulphide.

The viscous solution, after standing for some days (5 to 15), is filtered under pressure to remove the air and make a homogeneous mixture and is then squirted through tubes or holes, 0.05 to 0.2 mm. in diameter, under a pressure of 10 to 12 atmospheres. The material comes out in the form of threads which are at once passed through a liquid bath to wash the material and decompose the cellulose compound. The threads of cellulose produced by this decomposition are wound on spools or bobbins and dried. During the decomposition process the threads lose not only much of their strength and compactness, but also about 30 per cent. of their weight. Material made from these threads has many of the properties of natural silk. It has the peculiar rustle of silk and its brilliancy, but it is dyed with direct or cotton dyes. Some of

the threads of the artificial material are finer than those of the natural product and compare very favorably with the latter in strength; but most of the material used is of the coarser grades, being about twice the size of the natural silk thread. In the early days of the industry it seemed as if the threads would not find any use on account of their weakness, but this difficulty has been gradually overcome and the product has been constantly improved. This material has not displaced the natural silk but is sometimes mixed with it and is used for a large variety of articles, in many cases leading to the production of entirely new products. It has been used very extensively for making braid and for a heavy cloth, for the preparation of filaments for lamps, for dies, castings, etc. It has been in such demand that the output has been sold six months ahead. Some figures as to the growth and present condition of the industry will give an idea of its constantly increasing importance:

Year.	Amt. produced in kg.
1896	600,000
1906	1,700,000
1909	4,000,000

The production of the natural silk in 1909 has been estimated to be 20,000,000 kilograms, or only five times as much as that of the artificial product. J. Elliott Gilpin.

REVIEWS.

The Fundamental Principles of Chemistry. An Introduction to all Text-books of Chemistry. By Wilhelm Ostwald. Authorized translation by Harry W. Morse. New York, London, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. 349.

The aim of the book is thus stated by Ostwald in his preface: "Two tasks are set for the workers in any science. One of these is to enrich the chosen field by the discovery of new facts and the statement of new experiences. The other task is no less important, but its value is perhaps not so evident at first glance. It is to arrange the facts already known in the best order and to bring out the relations between them as clearly as possible. Whenever progress in the first of these tasks has been rapid, the second becomes the more necessary, for it offers the only possible way of attaining mastery over the manifold separate experiences and of bringing the science as

a whole into a convenient and serviceable form. * * *
The present book has for its object the presentation of the
actual fundamental principles of the science of chemistry,
their meaning and connection, as free as possible from ir-
relevant additions. * * * Questions concerning funda-
mental principles meet the teacher at every step, and the
mental character of the developing chemist is frequently de-
termined by the way in which they are answered. * * *
The book should be a guide to the teacher. It may serve to
show him how such generalizations are to be handled and
how they can be woven into his daily instruction in elementary
chemistry. Generalizations are the fundamental base of the
chemical symphony; and the various separate facts may be
varied according to need or desire. To make use of another
simile—generalizations are the bony skeleton of the chemical
body, and the teacher must always let the bones appear
through the individual chemical facts if he wishes to make
of his teaching a true work of art."

The book comprises eleven chapters. The first deals with
Bodies, Substances and Properties; the second with the Three
States; the third with Mixtures, Solutions and Pure Substances;
the fourth with Change of State and Equilibrium; the fifth
with Solutions; the sixth with Elements and Compounds;
the seventh with the Law of Combining Weights; the eighth
with Colligative Properties; the ninth with Reaction Velocity
and Equilibrium; the tenth with Isomorphism; and the eleventh
with the Ions.

This work, like every one that comes from the pen of this
great man, is full of suggestion and it is to be hoped that it
will be read by a large number of those for whom it was writ-
ten.

The work of the translator is admirably done.   H. C. J.

A Text-Book of Physiological Chemistry for Medical Students.
By John H. Long, M.S., Sc.D., Professor of Chemistry in Northwestern
University Medical School, Chicago. Second edition, revised. With
42 illustrations. Philadelphia: P. Blakiston's Son & Co. 1909. pp.
viii + 396. Price, $2.50.

The first part of this book deals with the various factors

concerned in digestion and metabolism, and the first four chapters are devoted to a consideration of the various nutritive substances, including the inorganic elements of water, air and salts. Another chapter is given up to a discussion of the carbohydrates and related bodies, and another to the fats and protein substances and their derivatives. In the next five chapters the author discusses the presence and action of ferments in the various organs and their relation to the different digestive processes.

The second part of the book deals with the various excretions of the body and gives different methods for their examination. Attention is called to the chemistry of the blood and various tissues, and the excretions of the various organs of the body, including all the more important end-products, are described at length. The author also devotes several chapters to the discussion of special topics, all of which are interestingly written. Perhaps the most interesting of these is the one which treats of the special properties of blood serum and its relation to immunity.

Although the author states in his preface that this book is intended to be a brief review of the important principles of physiological chemistry, in his endeavors to be brief he has not sacrificed any of the essential details necessary to a comprehensive understanding of the entire subject. The book is well written and not only appeals to the student of medicine but to all interested in physiological chemistry.

A MANUAL OF VOLUMETRIC ANALYSIS, Treating on the Subjects of Indicators, Test-papers, Alkalimetry, Including the Assay of Drugs by Titration, Acidimetry, Analysis by Oxidation and Reduction, Iodometry, Determinations by Precipitation, and by Color Comparison. By VIRGIL COBLENTZ, PH.D., PHARM.M., F.C.S., Professor of Chemistry in the New York College of Pharmacy. Second Edition, Revised, Completely Reconstructed and Enlarged, by ANTON VORISEK, PHAR.D., Professor of Analytical Chemistry in the College of Pharmacy, Columbia University. With 37 Illustrations. Philadelphia: P. Blakiston's Son & Co. 1909. pp. vii + 234. Price, $1.75.

This work now consists of a compact handbook primarily designed for the use of pharmacists. It comprises five chapters, the titles of which, as given, are "Introductory," "Determinations by Neutralization," "Determinations by Oxida-

tion and Reduction," "Determinations by Precipitation," and "Determinations by Comparison of Colors." An appendix contains atomic weight tables, and a list of elements and their most important compounds, with the molecular weights of the latter.

The procedures given are usually the better known and standard ones; the descriptions are concise but usually clear and reasonably adequate. Reactions are freely given, and calculations explained. The section on indicators is quite complete; that on ionic changes in solution is hardly adequate as a treatment of that subject. As a handy volume of sufficient scope to serve as a guide in the more frequently occurring lines of analysis, this work deserves the attention of pharmacists, for whom, as already stated, it is primarily written.   H. P. TALBOT.

RECHERCHES SUR LA PRÉPARATION ÉLECTROLYTIQUE DES COMPOSÉS DU PLOMB. Par CARL DUVIVIER, Ingénieur. Malines: L. et A. Godenne. 1909. pp. 19.

The electrolytic preparation of insoluble compounds from soluble anodes has so far been industrially successful only with lead. The pamphlet under notice deals with the research carried on by the author in the preparation of lead paints by the electrolytic solution of pure lead and its precipitation as basic carbonate, chromate, monoxide, sesquioxide and peroxide. While the preparation of white lead is carried on industrially according to the process of Luckow, the manufacture of other lead compounds by the aid of electrolysis of lead has so far been a commercial failure. The author reviews the white-lead processes of Hoosick, Luckow and Brown, which he has also tested, and then gives the detail of his own work, which is shown to have furnished good results.   H. O. HOFFMAN.

DIE ELECTROCHEMISCHEN VERFAHREN DER CHEMISCHEN GROSS-INDUSTRIE. Ihre Prinzipien und ihre Ausführung. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. I Band. Electrometallurgie wässriger Lösungen. Mit 117 Figuren und vielen Tabellen im Text. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1909. pp. vii + 284. Price, M. 12.

The present volume, dealing with the electrometallurgy

of aqueous solutions, is the first of a proposed series of four which is to cover the whole field of industrial electrochemistry; the three remaining volumes are to be entitled: Electrolysis of Aqueous Solutions with Insoluble Anodes; Electrolysis of Fused Salts; and Electric Furnaces. The aim of these publications is not only to describe the present state of the different electrochemical industries, but to discuss the processes critically according to principles of modern electrochemistry.

The volume under consideration treats of the metals copper, silver, gold, lead, zinc, tin (detinning tinplate), nickel, bismuth, cadmium, quicksilver, and the preparation of metallic compounds. It begins with a review of the electrolytic laws, which are sketched briefly and put in such a way as to be readily understood by the reader not fully at home in the ionic theory. The method chosen for presenting the electrometallurgy of the several metals is to take up first principles and then practice. Thus, in the electrolytic refining of metallic copper, the general principles are discussed under the heading of electrolysis of pure anodes; the behavior of impurities is then treated under impure anodes; a critical review of the matter in the two preceding sections furnishes the occasion for giving general rules that ought to govern practice; and lastly comes the consideration of efficiency. For the review of actual work, some leading examples of the multiple- and series-systems are given and a comparison of the two is made; then follows the working-up of fouled solutions and of anode-mud, and lastly comes a brief description of the necessary analytical determinations. The general plan of treatment is excellent and the same is true of the discussion of principles. The presentation of the practice cannot be praised so unreservedly. While many details of different plants are recorded in a systematic manner, others of importance are missing; of the 117 illustrations given in the text, in only one set (Figs. 103–106) are dimensions given; the photographic reproductions of parts of plants are so inferior as to have next to no value even as pictures.

In the second main division of copper, the electrolytic treatment of copper compounds, the processes of Marchesi, Hoepfner and Siemens are treated briefly, and with reason, as they have been failures; but there is no mention of the successful electrolysis of pure copper matte with the recovery of sulphur as carried out in the Mansfeld district. Of the electrolytic production of articles of commerce (tubes, etc.), probably too little is known at large to make the third and last division comprehensive.

In the parting of doré silver, also, many important details, descriptive as well as constructive, which are available through the technical literature deserve to be mentioned. In the recovery of gold from cyanide solutions the practice of Siemens and Halske, as described in the book of von Uslar in 1903, and reproduced here, has been considerably modified and supplemented. Similar remarks might be made regarding some of the remaining metals.

Taking the book as a whole, there is presented a volume which is excellent in arrangement, in presentation of principles, and in discussion of processes from the point of view of modern electrochemistry; the treatment of actual practice requires some revision to bring it to the standard of that of principles. The electrochemist makes himself felt everywhere in the book, the engineer is less evident. The metallurgist will find the volume the best guide that has been presented so far for the study of principles of the various electrolytic processes he may have to deal with; the electrochemist will obtain a better introduction into actual practice than is usually furnished in books dealing with the subject.

H. O. HOFMAN.

AMERICAN

CHEMICAL JOURNAL

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC ZINC COMPOUNDS.

By E. P. Kohler and Gertrude L. Heritage.

This investigation was made in continuation of a study of unsaturated compounds that contain the chain C : C.C : O. As stated in a recent paper,[1] we have found it difficult to determine the relation between the character of organic magnesium compounds and their mode of addition to ketones that have this chain. The results published in earlier papers indicate that, in the case of a ketone which gives both 1,2- and 1,4-addition products with organic magnesium compounds, the relative amounts of these products depend upon the chemical rather than the spatial character of the hydrocarbon residue in the magnesium compound.

The results also show, however, a marked difference in the mode of addition of magnesium compounds that contain alkyl groups and those derived from aromatic halogen compounds which have the halogen in direct union with the nucleus. All of the former give practically the same amount of 1,4-addition product with any one ketone, while phenyl-magnesium bromide and tolylmagnesium bromide invariably give relatively much more 1,2-addition product. It was im-

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[1] This Journal, **43**, 412.

portant, therefore, to try other types of halogen compounds in order, if possible, to find an explanation for this difference in the behavior of aliphatic and aromatic derivatives.

We tried magnesium compounds obtained from bromine substitution products of unsaturated cyclic hydrocarbons, intermediate between hexamethylene and aromatic compounds, but found that these lost hydrobromic acid so readily that the results are ambiguous. We have also tried phenyl-acetylenemagnesium bromide, but thus far have failed to find any satisfactory method for separating the products.

As the halogen substitution products of hydrocarbons did not serve our purpose, we turned to the corresponding derivatives of esters. The work of Zeltner on the reaction between magnesium and α-brom esters showed that it would be useless to attempt to carry out the reaction in the usual way—first making an ethereal solution of the magnesium compound and then adding the ketone. But it seemed possible that in certain selected cases the same end might be accomplished by allowing magnesium to react with the brom ester in the presence of the unsaturated compound.

Experiments in this direction disclosed a new difficulty. The magnesium derivatives formed in this way are sparingly soluble in ether, and they separate in the form of heavy viscous liquids that effectively protect the metal from further reaction. Consequently, in order to complete the reaction, it is necessary to boil the mixture for days and to use a large excess of magnesium and brom ester. The reaction proceeds more rapidly when benzene is substituted for ether as a medium, because the magnesium derivatives are less viscous at the temperature of boiling benzene; but even under these conditions it is almost impossible to complete the reaction.

A simple way out of the difficulty was found in the substitution of zinc for magnesium. The reaction between zinc, a brom ester, and an unsaturated compound was used by Jaworsky and Reformatzky,[1] and later also by Rupe and Lotz,[2] for making homologues of sorbic acid. The former used crotonic aldehyde, the latter mesityl oxide; as both of

[1] Ber. d. chem. Ges., **35**, 3633.
[2] *Ibid.*, **36**, 15.

these unsaturated compounds give exclusively 1,2-addition products with all Grignard reagents, the results of these investigators shed no light on our problem.

We have tried the same reaction with a number of unsaturated ketones that give only saturated compounds when treated with Grignard reagents and have found that all of these give unsaturated β-hydroxy esters when they react with zinc and bromacetic ester. Moreover, ketones, like benzaldesoxybenzoin and benzalacetomesitylene, which have a very unreactive carbonyl group, do not react with zinc and brom ester, although they give an excellent yield of 1,4-addition product with Grignard reagents. The mode of addition of organic zinc compounds derived from α-brom esters is, therefore, different from that of any Grignard reagent that has hitherto been used. The difference is illustrated by the following equations:

I. $C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr =$
$$(C_6H_5)_2CHCH : C(OMgBr)C_6H_5 \longrightarrow$$
$$(C_6H_5)_2CHCH_2COC_6H_5.$$

II. $C_6H_5CH : CHCOC_6H_5 + BrZnCH_2CO_2CH_3 =$
$$\underset{\overset{|}{CH_2CO_2CH_3}}{C_6H_5CH : CHC(OZnBr)C_6H_5} \longrightarrow$$
$$\underset{\overset{|}{CH_2CO_2CH_3}}{C_6H_5CH : CHCOHC_6H_5} .$$
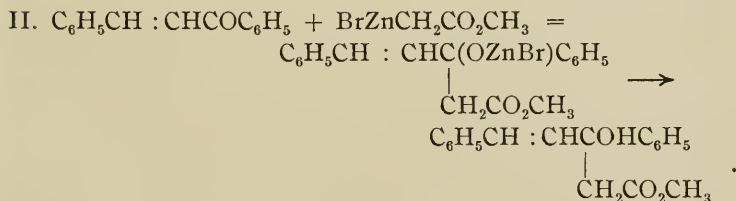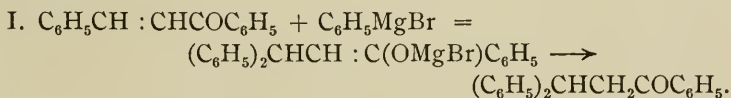
Our results show that the difference between these reactions is due solely to the nature of the halogen compounds used. For although metal, solvent, and procedure, as well as halogen compound, are different from those used in the case of Grignard reagents, it has been possible to prove by direct experiments that these do not influence the mode of addition. With benzalpropiophenone, for example, it was possible to carry out reactions with brombenzene and methyl bromacetate in exactly the same way, and to use the same metal and the same medium; but one gave only saturated ketones, the other only unsaturated ester:

I. $C_6H_5CH : C(CH_3)COC_6H_5 + C_6H_5Br + Mg \longrightarrow$
$$(C_6H_5)_2CHCH(CH_3)COC_6H_5.$$

II. $C_6H_5CH : C(CH_3)COC_6H_5 + BrCH_2CO_2CH_3 + Mg \longrightarrow$
$$C_6H_5CH : C(CH_3)COHC_6H_5$$
$$\underset{CH_2CO_2CH_3}{\mid} .$$
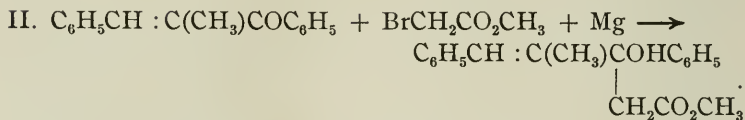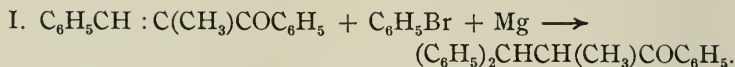
The fact that the zinc derivatives of α-brom esters combine only with the carbonyl group explains the unusually good yields obtained by this reaction, since earlier work has shown that only those metallic derivatives which are formed by 1,4-addition are capable of combining with a second molecule of unsaturated ketones to form complex products. In addition to its theoretical interest this reaction, therefore, has practical value in that it supplies an excellent method for making important classes of unsaturated compounds. The acids that, heretofore, have been made by condensing cinnamic aldehyde with sodium salts of acids are more quickly made by using zinc and a brom ester, and in all the cases in which we have tried it, the latter method gave a much better yield than the former. Moreover, since it is easy to get a great number and variety of unsaturated ketones and brom esters, it is possible, by this method, to make acids with almost any desired number and arrangement of hydrocarbon residues about the chain C : C.C : C.C : O.

This paper contains only the results obtained with esters of bromacetic acid, but the same reaction takes place with bromine substitution products of much more complex esters. Thus benzalacetophenone and bromisobutyric ester give an unsaturated hydroxy ester in accordance with the equation:

$C_6H_5CH : CHCOC_6H_5 + BrZnC(CH_3)_2CO_2C_2H_5 \longrightarrow$
$$C_6H_5CH : CHCOHC_6H_5$$
$$\underset{(CH_3)_2CCO_2C_2H_5}{\mid} .$$
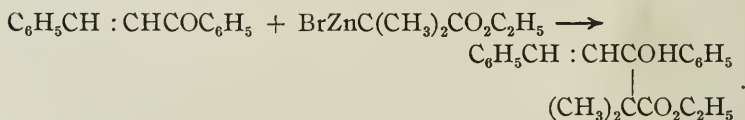
Although Jaworsky and Reformatsky state that water cannot be eliminated from unsaturated hydroxy esters that do not have hydrogen in the α position, we expect to be able to show in an early paper that these substances can be used for

making acids derived from allene that at present can be made in no other way.

<div align="center">EXPERIMENTAL PART.</div>

I. Experiments with Benzalacetophenone and Benzalpropiophenone.

The experiments with these two ketones were performed with special care for the purpose of determining whether more than one product is formed, and whether the results can be attributed to anything else than the chemical character of the bromine compound.

Benzalacetophenone, Methyl Bromacetate, and Zinc.—A slight excess of zinc was added to a solution of equivalent quantities of the ketone and ester in benzene. The reaction was started by warming gently over the free flame, then allowed to proceed as long as the liquid continued to boil, and finally completed by heating in a water bath for an hour. The clear solution was poured into water, the basic zinc salts removed with acid, and the benzene layer diluted with an equal volume of ether. This precipitated a colorless, crystalline solid. After filtering and washing the solid with ether, the filtrate was allowed to evaporate in a draught. It deposited more of the same solid and a small quantity of liquid that attacked the eyes. The mixture was filtered, the solid washed with ligroin containing a small quantity of ether, and the filtrate shaken with potassium hydroxide for the purpose of removing any brom ester present. The ether-ligroin layer was then dried and distilled from a water bath; it left only a drop of yellow liquid.

The solid was purified by recrystallization from a mixture of acetone and alcohol.

Analysis:

0.1245 gram substance gave 0.4011 gram CO_2 and 0.0780 gram H_2O.

	Calculated for $C_{18}H_{18}O_3$.	Found.
C	76.60	76.8
H	6.34	6.1

The composition of the substance shows that it is formed by condensation of one molecule of ester with one of the unsaturated ketone. Calculated on this basis, the total amount of pure solid obtained represented 98 per cent. of the benzalacetophenone used.

Only two formulas for this substance need to be considered. It is either an unsaturated hydroxy ester (I) formed by 1,2-addition, or a saturated ketonic ester (II) resulting from 1,4-addition:

$$C_6H_5CH : CHCOHC_6H_5 \qquad\qquad C_6H_5CHCH_2COC_6H_5$$
$$\mid \qquad\qquad\qquad\qquad\qquad\qquad \mid$$
$$CH_2CO_2CH_3 \qquad\qquad\qquad CH_2CO_2CH_3$$
$$\text{I.} \qquad\qquad\qquad\qquad\qquad \text{II.}$$
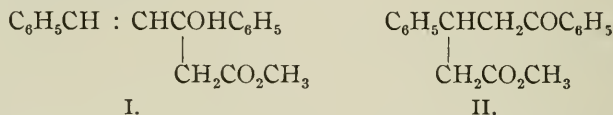
Between the two it was easy to decide by oxidation experiments. The substance readily reduced permanganate dissolved in acetone and the sole organic product was benzoic acid; 2.8 grams of substance gave 2.2 grams of pure benzoic acid—approximately two molecules of acid for one of substance. The substance is therefore the unsaturated hydroxy ester formed by 1,2-addition.

Methyl β-Hydroxy-β-phenyl-γ-benzalbutyrate,
$C_6H_5CH : CHCOH(C_6H_5)CH_2CO_2CH_3$, crystallizes in fine needles that melt at 126°. It is sparingly soluble in ligroin, moderately in ether and alcohol, readily in acetone and chloroform.

Methyl β-Hydroxy-β-phenyl-γ-benzal-δ-brombutyrate,
$C_6H_5CBr : CHCOH(C_6H_5)CH_2CO_2CH_3$.—The unsaturated hydroxy ester rapidly combines with bromine. A solution in dry carbon bisulphide was cooled in a freezing mixture and treated with dry bromine as long as the color was discharged immediately. No evolution of hydrobromic acid was observed during the process and the solid left on evaporating the solvent liberated iodine from an alcoholic solution of potassium iodide—it therefore contained two bromine atoms in combination with adjoining carbon atoms. The substance obtained by recrystallizing this solid from chloroform and alcohol, however, contained only one atom of bromine to the molecule. It is sparingly soluble in alcohol, ether,

and cold chloroform, moderately in boiling chloroform. It separates from solution in thick needles that begin to decompose at about 200°.

Analysis:

0.3671 gram substance gave 0.3642 gram CO_2 and 0.0675 gram H_2O.

	Calculated for $C_{18}H_{17}O_3Br$.	Found.
C	59.44	59.8
H	4.50	4.7

As the substance is formed by loss of hydrobromic acid from a dibrom addition product of methyl phenylhydroxybenzalbutyrate it must be either a γ- or a δ-bromine substitution product of this ester. The γ-bromine substitution product can be made by direct synthesis, starting with α-brombenzalacetophenone:

$$C_6H_5CH : CBrCOC_6H_5 + CH_2BrCO_2CH_3 + Zn + [H_2O] =$$
$$C_6H_5CH : CBrCOH(C_6H_5)$$
$$| \quad\quad + Zn(OH)Br.$$
$$CH_2CO_2CH_3$$
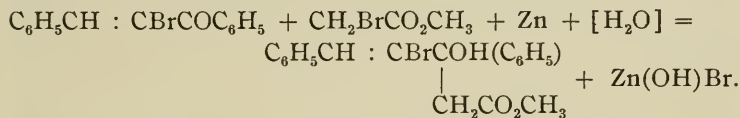
The product of this reaction was isomeric with the substance in question. The latter is, therefore, a δ-bromine derivative.

Magnesium can be used in place of zinc in the reaction between benzalacetophenone and methyl bromacetate without materially changing the result; the principal product is the same and, when benzene is used as solvent, the yield is fair—about 80 per cent. of the calculated quantity. The smaller yield is due to the fact that organic magnesium compounds combine more readily than the corresponding zinc compounds with the carbonyl group of esters. In the experiments with magnesium we found, accordingly, that part of the methyl bromacetate was condensed to a substance that gave a color reaction with ferric chloride—acetacetic ester, probably—and that some of the benzalacetophenone was left after all of the brom ester had disappeared.

That magnesium, like zinc, gives no 1,4-addition product was established by the following experiment. A reaction

with 10.4 grams of benzalacetophenone, 10 grams of methyl bromacetate, and 2 grams of magnesium, was carried out in benzene, and the magnesium salts removed in the usual way. The solution in benzene, containing all the organic products of the reaction, was dried and distilled from a water bath. The residue, dissolved in acetone and oxidized with potassium permanganate, gave 11.9 grams of benzoic acid—almost exactly two molecules of acid for one of benzalacetophenone used. Not a trace of any other acid could be detected.

By using magnesium in place of zinc, it is possible to substitute ether for benzene as solvent; but the manipulation is troublesome and the yield at best unsatisfactory. The reaction is easily started, but soon stops, because the product separates as a viscid oil that completely envelops the metal. It can be started again by pouring off the ethereal layer and adding to it fresh magnesium, and by repeating this operation 4 or 5 times much of the benzalacetophenone can be utilized.

When the viscid product is decomposed with water and acid it gives, principally, the same unsaturated hydroxy ester that was obtained in previous experiments. The best yield obtained was only 60 per cent. of the possible amount. The yield is so small because a part of the unsaturated ketone escapes reaction and not because of any 1,4-addition. This was established as in previous cases by oxidizing everything left at the end of the reaction with potassium permanganate dissolved in acetone. The mixture of products and unchanged ketone from 5.2 grams of unsaturated compound gave 6 grams of benzoic acid. No other organic product of oxidation could be detected.

The experiments that have been described proved that neither the metal nor the solvent is responsible for the difference in the mode of addition of the zinc compounds of brom esters and that of the ordinary Grignard reagents. It now remained to be determined whether this difference is due to the method of procedure or to the character of the halogen compound. Metallic derivatives of brom esters corresponding to the simple Grignard reagents cannot be made, but with

some ketones it is possible to use a simple halide and magnesium in place of the Grignard reagent.

In the reaction between Grignard reagents and benzalpropiophenone, for example, the presence of the methyl group in the α position of the ketone prevents the formation of complex products.[1] In the case of this ketone, therefore, it was possible to compare the results obtained by adding the ketone to excess of phenylmagnesium bromide in the usual way with those obained by adding magnesium to an ethereal solution of equivalent quantities of the ketone and brombenzene. We found that both methods of procedure gave the same product—β,β-diphenylbutyrophenone formed by 1,4-addition. The ketone reacts much more slowly with magnesium and the halogen compound than with the corresponding Grignard reagent, and the result is affected to a much greater extent by impurities in the reagents; but with pure substances and ether freshly distilled from sodium the yield is equally good in both cases. Not a trace of benzoic acid was obtained when the entire product of the reaction was treated with a solution of potassium permanganate. There was, therefore, no 1,2-addition.

The result was quite different when methyl bromacetate was used in place of brombenzene. The sole product of the reaction was readily oxidized to benzoic acid, and it combined with bromine at the temperature of a freezing mixture. It is, therefore, an unsaturated hydroxy ester formed by 1,2-addition.

Methyl β-hydroxy-β-phenyl-γ-methyl-γ-benzalbutyrate,
$C_6H_5CH : C(CH_3)COH(C_6H_5)CH_2CO_2CH_3$, the product obtained from benzalpropiophenone and methyl bromacetate, both with zinc and benzene and with magnesium in ether, is a colorless solid melting at 70°. It is readily soluble in all the common organic solvents except ligroin. It was purified from a mixture of methyl alcohol and ligroin, from which it separated in large glistening plates.

Analysis:

0.1411 gram substance gave 0.3970 gram CO_2 and 0.0890 gram H_2O.

[1] THIS JOURNAL, **34**, 568.

	Calculated for $C_{19}H_{20}O_3$.	Found.
C	77.0	76.7
H	6.8	7.0

II. Experiments with Other Unsaturated Compounds.

The same procedure was used in all the following experiments. The unsaturated compound and 10 per cent. more than the equivalent quantity of brom ester were dissolved in dry benzene and the calculated amount of zinc, in the form of shavings, added to this solution. The reaction was started by warming over a free flame, then allowed to proceed without further heating as long as the benzene continued to boil, and finally completed by boiling in a water bath until all the metal disappeared. In most cases everything remained in solution. The clear, colorless or pale yellow liquid was poured into water and the basic zinc salts dissolved by shaking with dilute acid. The solution in benzene was then dried with fused calcium chloride, the benzene removed by distillation or evaporation in a draught and the residue purified by crystallization if solid, or distillation under diminished pressure if liquid. The yield was excellent—never less than 90 per cent., and occasionally, when the product was solid, over 95 per cent. of the possible quantity.

Methyl β-Hydroxy-β-phenyl-γ-ethylidenebutyrate,
$CH_3CH : CHCOH(C_6H_5)CH_2CO_2CH_3$.—For reasons given elsewhere, ethylidenacetophenone gives 1,4-addition products more readily than any other unsaturated compound except vinylphenyl ketone. With methyl bromacetate and zinc, however, the sole product is an unsaturated hydroxy ester formed by 1,2-addition. The ester was purified by recrystallization from ligroin and thus obtained in long needles melting at 58°. It is readily soluble in common organic solvents except ligroin.

Analysis:

0.1137 gram substance gave 0.2960 gram CO_2 and 0.0742 gram H_2O.

	Calculated for $C_{13}H_{16}O_3$.	Found.
C	70.9	71.00
H	7.3	7.25

Methyl β-Hydroxy-β-phenyl-γ-ethylidene-δ-brombutyrate,
$CH_3CBr : CHCOH(C_6H_5)CH_2CO_2CH_3$.—The unsaturated ester, dissolved in carbon bisulphide, readily combines with bromine and it is possible to remove the solvent without loss of hydrobromic acid; but all efforts to purify the dibromide failed. The crude product, washed with carbon bisulphide and dried, gave results more than 1 per cent. too high in carbon, and when it was redissolved in carbon bisulphide and precipitated with ligroin, the monobromide separated. This was recrystallized from alcohol. It separated in small prisms or plates that melted, with decomposition, at about 175°. The structural formula given above is based on the assumption that the loss of hydrobromic acid from the dibromide takes place in the same way as from the dibromide of methyl benzalphenylhydroxybutyrate.

Analysis:

0.1475 gram substance gave 0.2823 gram CO_2 and 0.0740 gram H_2O.

	Calculated for $C_{13}H_{15}O_3Br$.	Found.
C	52.1	51.5
H	5.0	5.5

Methyl Cinnamylideneacetate, $C_6H_5CH : CH.CH : CHCO_2CH_3$. —The product obtained from cinnamic aldehyde did not solidify when the solvent was evaporated. It was, therefore, distilled under diminished pressure. It began to lose water freely at about 160°. At 185° (20 mm.) it yielded a colorless distillate that solidified in the receiver. After one recrystallization from methyl alcohol, the solid melted at 71°—the melting point of the methyl ester of cinnamylidenacetic acid. A similar experiment with cinnamic aldehyde and α-brompropionic ester gave an excellent yield of the corresponding ester of α-methylcinnamylidenacetic acid. It is probable, therefore, that all the hydroxy acids obtained with cinnamic aldehyde lose water with the same ease.

Ethyl β-Methyl-β-hydroxy-γ-benzalbutyrate,
$C_6H_5CH : CHCOH(CH_3)CH_2CO_2C_2H_5$.—The product obtained

from benzalacetone and ethyl bromacetate distilled under diminished pressure without loss of water. It is a colorless liquid that boils at 192° (20 mm.).

Analysis:

0.1390 gram substance gave 0.3654 gram CO_2 and 0.0998 gram H_2O.

	Calculated for $C_{14}H_{18}O_3$.	Found.
C	71.8	71.7
H	7.7	8.0

The ester is hydrolyzed with difficulty. When poured into strong aqueous potassium hydroxide (1 : 3) it soon dissolves; the colorless solution becomes hot, then turns yellow, and, on cooling, red. When this solution is diluted it deposits a brown liquid that partially solidifies on cooling with ice water. The diluted liquid was extracted with ether and the aqueous layer acidified, but it was found free from organic acids. The ethereal layer was dried, the ether removed, and the residue distilled with steam. This gave a colorless liquid that solidified in the receiver. After one crystallization the solid melted sharply at 37°.

Analysis:

0.1173 gram substance gave 0.3933 gram CO_2 and 0.0885 gram H_2O.

	Calculated for $C_{11}H_{12}$.	Found.
C	91.7	91.4
H	8.3	8.4

The substance is methylphenylbutadiene, formed by loss of water and carbon dioxide from the hydroxy acid:

$$C_6H_5CH : CHCOH(CH_3)CH_2CO_2H =$$
$$C_6H_5CH : CHC(CH_3) : CH_2 + H_2O + CO_2.$$
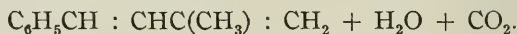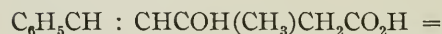
The same hydrocarbon was obtained by Grignard by the action of methylmagnesium iodide on cinnamic aldehyde. The melting point given in Grignard's paper is 27°, but this is probably a printer's error, because a specimen prepared by Grignard's method and purified by distillation was found to be identical with our product.

β-Methylcinnamylidenacetic Acid,

$C_6H_5CH : CHC(CH_3) : CHCO_2H$.—When the unsaturated hydroxy ester is boiled with hydrochloric acid (1 : 3) it loses water more rapidly than it is hydrolyzed. The product obtained by boiling 20 grams of the ester with 500 cc. of acid for 8 hours contained less than a gram of acid. It was separated from the water, dissolved in a 3 per cent. solution of potassium hydroxide in methyl alcohol, and the solution allowed to stand at the ordinary temperature until no precipitation occurred, when it was poured into water. The acid obtained in this way was purified by recrystallization from methyl alcohol. It separated in small prisms or plates that melted at 153°.

Analysis:

0.1175 gram substance gave 0.3289 gram CO_2 and 0.0687 gram H_2O.

	Calculated for $C_{12}H_{12}O_2$.	Found.
C	76.6	76.34
H	6.4	6.50

Methyl β-Butylcinnamylidenacetate,

$C_6H_5CH : CHC[C(CH_3)_3] : CHCO_2CH_3$.—The product obtained from benzalpinacolin and methyl bromacetate lost water on distillation under diminished pressure. The resulting ester is a colorless liquid that boils at 210° (20 mm.).

Analysis:

0.1305 gram substance gave 0.3756 gram CO_2 and 0.1002 gram H_2O.

	Calculated for $C_{16}H_{20}O_2$.	Found.
C	78.7	78.5
H	8.2	8.5

Methyl β-Hydroxy-β-phenyl-γ-brom-γ-benzalbutyrate,

$C_6H_5CH : CBrCOH(C_6H_5)CH_2CO_2CH_3$.—This substance was made from α-brombenzalacetophenone and methyl bromacetate for the purpose of locating the bromine in the product obtained by eliminating hydrobromic acid from the dibromide of methyl β-hydroxy-β-phenyl-γ-benzalbutyrate. It was

purified by recrystallization from alcohol; colorless needles melting at 79°–80°. On oxidation with potassium permanganate, in acetone, it gave 2 molecules of benzoic acid for each molecule of ester.

Analysis:

0.1288 gram substance gave 0.2829 gram CO_2 and 0.0520 gram H_2O.

	Calculated for $C_{18}H_{17}O_3Br$.	Found.
C	59.8	59.9
H	4.7	4.5

Methyl β-Hydroxy-β-phenyl-γ-cinnamylidenebutyrate,.
$C_6H_5CH : CH.CH : CHCOH(C_6H_5)CH_2CO_2CH_3$.—No difficulty was experienced in applying the reaction to cinnamylidenacetophenone; it was easily started and completed, and it gave the usual yield. The resulting hydroxy ester was purified by recrystallization from acetone and alcohol—fine needles melting at 112°.

Analysis:

0.1210 gram substance gave 0.3461 gram substance and 0.0677 gram H_2O.

	Calculated for $C_{20}H_{20}O_3$.	Found.
C	77.9	78.0
H	6.5	6.2

The only unsaturated ketones tried without success were benzaldeoxybenzoin and benzalacetomesitylene. When a solution of a mixture of methyl bromacetate and either of these ketones in benzene is boiled with zinc, the metal slowly disappears but the unsaturated compound does not enter into the reaction. The gelatinous zinc derivative that separates after prolonged boiling gives only oily products when decomposed with acids, and neither benzoic nor any other aromatic acid is obtained when these products are oxidized. Most of the unsaturated ketone can be recovered by evaporating the benzene. It is evident that in these cases condensation of the ester takes place more rapidly than addition to the unsaturated ketone. As these ketones readily give 1,4-addi-

tion products with Grignard reagents, it is safe to conclude that this mode of addition cannot take place with the zinc derivatives of brom esters.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
February, 1910.

STUDIES IN ESTERIFICATION:
THE ESTERIFICATION OF THIOLBENZOIC ACID BY ALCOHOL AND OF BENZOIC ACID BY MERCAPTAN.

BY E. EMMET REID.

One of the most important, and also one of the most extensively studied, reactions in organic chemistry is esterification, and yet, according to Baly and Schaefer,[1] "the actual mechanism of esterification is imperfectly understood, although the most generally accepted view is that the reaction is one of addition of the alcohol, followed by the loss of water." This idea was put forward by Henry[2] in opposition to Friedel's[3] suggestion that, in the presence of hydrochloric acid, an acid chloride is formed which acts as an intermediate product in the formation of ester. Friedel's explanation could not apply in the absence of hydrochloric acid, and Henry's attempt to account for the accelerating action of this substance was awkward, yet both ideas have been in continuous use up to the present time. Angeli,[4] Wegscheider,[5] Claisen,[6] von Pechmann,[7] Stieglitz,[8] and many others have used Henry's hypothesis, while Friedel's has had many defenders. The textbooks give sometimes the one, sometimes the other, and frequently both.

Assuming that the reaction between benzoic acid and alcohol takes place according to Henry's hypothesis, we have, according as the alcohol adds as $H-OC_2H_5$ or as $HO-C_2H_5$,

[1] J. Chem. Soc., **93**, 1810.
[2] Ber. d. chem. Ges., **10**, 2041.
[3] Compt. Rend., **68**, 1557.
[4] Ber. d. chem. Ges., **29**, Ref. 591.
[5] *Ibid.*, **28**, 1468; **29**, 2301.
[6] *Ibid.*, **20**, 649.
[7] *Ibid.*, **31**, 501.
[8] J. Am. Chem. Soc., **32**, 225.

equation (1) or (2). For convenience in following the reaction the oxygen atoms are marked O′, O″, O‴.

$$(1) \quad C_6H_5C\!\!<\!\!\begin{array}{l}O'H\\O''\end{array} \;+\; \begin{array}{c}H\\|\\O'''C_2H_5\end{array} \;\rightleftarrows\; C_6H_5C\!\!<\!\!\begin{array}{l}O'H\\O''H\\O''C_2H_5\end{array} \;\rightleftarrows$$

$$C_6H_5C\!\!<\!\!\begin{array}{l}O''\\O'''C_2H_5\end{array} \;+\; H_2O'.$$

$$(2) \quad C_6H_5C\!\!<\!\!\begin{array}{l}O'H\\O''\end{array} \;+\; \begin{array}{c}C_2H_5\\|\\O''H\end{array} \;\rightleftarrows\; C_6H_5C\!\!<\!\!\begin{array}{l}O'H\\O'''H\\O''C_2H_5\end{array} \;\rightleftarrows$$

$$C_6H_5C\!\!<\!\!\begin{array}{l}O'''\\O''C_2H_5\end{array} \;+\;H_2O'.$$
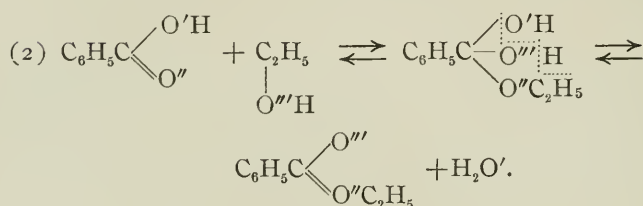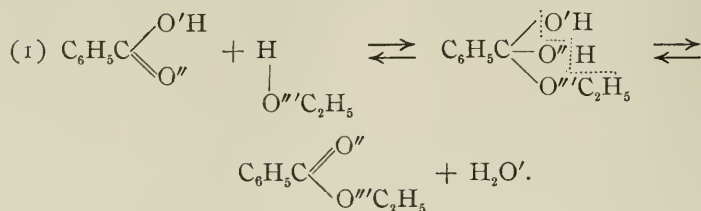
In neither case does O′, the hydroxyl oxygen of the acid, appear in the ethoxyl group of the ester. If the alcohol added as H– and –O‴C₂H₅, O‴, the hydroxyl oxygen of the alcohol, would appear in the ethoxyl group of the ester, but if the alcohol should add as HO‴— and —C₂H₅ this O‴ would not so occur in the ester. No supposition need here be made as to whether the alcohol breaks up before or during the act of addition, or as to whether that breaking up is electrolytic or not. Since in equation (1) O′ and O″ occupy exactly equivalent positions in the two hydroxyl groups of the assumed intermediate product, it would be a matter of chance whether O′ or O″ is eliminated as water. An exactly similar statement can be made concerning O′ and O‴ in equation (2).

It is, of course, impossible to distinguish oxygen atoms from each other when oxygen acids and oxygen alcohols are employed, but when esterification is carried on between compounds containing sulphur atoms, we may keep track of the oxygen atoms O′ and O‴ by replacing the one or the other by a sulphur atom. Thionbenzoic acid, C_6H_5CSOH, having

a sulphur atom in the place of O″, has been described by Fleischer,[1] but its existence has been rendered doubtful by Klinger.[2] I have repeated much of the work and am convinced that Fleischer's observations are erroneous. In thiolbenzoic acid, O′ is replaced by a sulphur atom. Substituting these sulphur acids in equations (1) and (2) we have:

$$(1') \quad C_6H_5C \begin{matrix} SH \\ \diagdown \\ O \end{matrix} + \begin{matrix} H \\ | \\ OC_2H_5 \end{matrix}$$

$$(2') \quad C_6H_5C \begin{matrix} SH \\ \diagdown \\ O \end{matrix} + \begin{matrix} C_2H_5 \\ | \\ OH \end{matrix}$$

$$C_6H_5C \begin{matrix} SH \\ \diagdown \\ OC_2H_5 \end{matrix} \rightleftharpoons \begin{matrix} C_6H_5C \diagup^O_{OC_2H_5} + H_2S. \\ C_6H_5C \diagup^S_{OC_2H_5} + H_2O. \end{matrix}$$
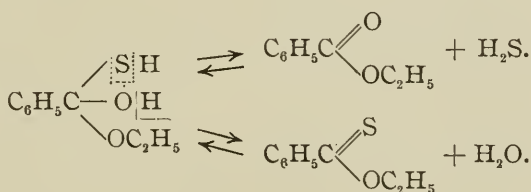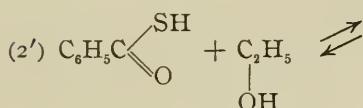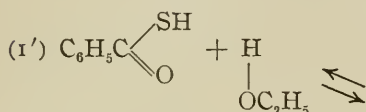
It is obvious that the assumed intermediate compound is the same in both cases and that this complex might break down into ethyl benzoate and hydrogen sulphide, or into ethyl thionbenzoate, $C_6H_5CSOC_2H_5$, and water, depending on the relative changes in energy, but ethyl thiolbenzoate, $C_6H_5COSC_2H_5$, could not be formed.

In the esterification of benzoic acid by mercaptan, a sulphur atom takes the place of O‴. Equations (1) and (2) thus become:

$$(1'') \quad C_6H_5C \begin{matrix} OH \\ \diagdown \\ O \end{matrix} + \begin{matrix} H \\ | \\ SC_2H_5 \end{matrix} \rightleftharpoons C_6H_5C \diagup^{OH}_{SC_2H_5}\diagdown^{OH} \rightleftharpoons$$

$$C_6H_5C \diagup^O_{SC_2H_5} + H_2O.$$
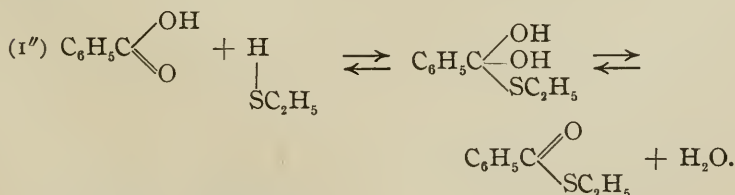
[1] Ann. Chem. (Liebig), **140**, 236.
[2] Ber. d. chem. Ges., **15**, 861.

$$(2'') \quad C_6H_5C{\overset{OH}{\underset{O}{\diagdown}}} \quad + \quad C_2H_5 \atop | \atop SH \qquad \rightleftharpoons$$

$$C_6H_5C{\overset{O\,H}{\overset{|\cdots}{\underset{OC_2H_5}{\diagup}}}}\,S\,H \qquad \overset{\rightleftharpoons}{} \qquad C_6H_5C{\overset{O}{\underset{OC_2H_5}{\diagdown}}} \quad + \quad H_2S.$$

$$\underset{\rightleftharpoons}{} \qquad C_5H_5C{\overset{S}{\underset{OC_2H_5}{\diagdown}}} \quad + \quad H_2O.$$

According to (1″) the products should be ethyl thiolbenzoate and water, while if (2″) correctly represents the reaction, either ethyl thionbenzoate and water, or ethyl benzoate and hydrogen sulphide, should be formed. Since the intermediate complex is the same in (2″) as in (1′) and (2′), the same reasoning applies in this case.

By reasoning exactly analogous to this, O. Wallach[1] explained the numerous observations of Salomon[2] on the saponification of the esters of the various thiocarbonic acids. Schmidt and Glutz,[3] Englehardt, Latschinoff, and Malyscheff,[4] Schiller and Otto,[5] Tüttscheff,[6] Michler,[7] Morley and Saint,[8] and Jones and Tasker[9] have all obtained results on the saponification of various thiol esters which may be readily explained in a similar way.

The present work was undertaken to test the above suggestions. Besides this, it was of even greater interest to find out in what manner and to what extent mercaptan may form esters. Though mercaptans have, since their discovery, been considered as the analogues of the alcohols, nothing has been known as to their direct esterification.

The experiments have been both qualitative and quantitative.

[1] Ber. d. chem. Ges., **13**, 530.
[2] J. prakt. Chem., [2] **6**, 433; **8**, 114.　Ber. d. chem. Ges., **8**, 1506.
[3] Ber. d. chem. Ges., **1**, 166.
[4] Z. Chem., **1868**, 353.
[5] Ber. d. chem. Ges., **9**, 1635.
[6] Jahres. d. Chem., **1863**, 483.
[7] Ann. Chem. (Liebig), **176**, 177.
[8] J. Chem. Soc., **43**, 400.
[9] *Ibid.*, **95**, 1904 and 1910.

Materials.

Thiolbenzoic Acid.—This was made according to Kym's[1] directions. After being distilled with steam, it was dissolved in ammonia, and precipitated, in crystalline form, from cold solution. The crystalline acid was kept over sulphuric acid in a rarefied atmosphere of hydrogen for a week before use. It must have occluded some water and may have contained some benzoic acid. It is not a satisfactory compound with which to work.

Ethyl Benzoate.—This ester, made from the acid and very pure alcohol, was well washed with water and dilute ammonia and then ten times with large volumes of water, and thoroughly dried. On distilling through a Hempel tube, nearly all of it went over with a variation of the boiling point of only about $0°.1$. It boiled at $213°.1$ (cor.) at 757.5 mm. and had a density $(25°/25°)$ of 1.0448. This boiling point is higher and the density less than the values usually given for these constants.

Ethyl Thiolbenzoate.—This was made according to the directions of Wheeler,[2] from potassium thiolbenzoate prepared by Kym's method. On the sixth fractionation the bulk of it went over between $252°$ and $253°$ (cor.) at 763 mm. This boiling point agrees with that given by Wheeler, $252°$–$254°$. Its density $(25°/25°)$ was 1.0971.

Mercaptan.—This was prepared in the usual way from sodium ethyl sulphate. Some increase over the recorded yield was obtained by adding a half-liter of ordinary alcohol to the sulphuric acid mixture after the liter of absolute alcohol had been put in. The product was freed from sulphide by the usual treatment with caustic soda and dried for a long time over anhydrous potassium carbonate. The fraction passing over between $35°$ and $37°$ was again dried and redistilled. The fraction boiling between $35°.5$ and $36°.1$ was used.

The *benzoic acid* used in the quantitative work was Kahl-

[1] Ber. d. chem. Ges., **32**, 3533. Note.
[2] This Journal, **24**, 69.

baum's best. The *alcohol* was absolutely anhydrous. The *water* was conductivity water of high purity.

Thiolbenzoic Acid and Alcohol.

Though thio esters are readily made by alkylating the salts of thio acids[1] and from acid chlorides and mercaptans or metallic mercaptides,[2] no thio esters have ever been made from free thiol acids. Engelhardt, Latschinoff, and Malyscheff[3] passed hydrochloric acid into an alcoholic olution of potassium thiolbenzoate and obtained ethyl benzoate and hydrogen sulphide. Evidently the esterification of the thiol acid set free proceeded according to the equation:

$$(3) \quad C_6H_5COSH + HOC_2H_5 = C_6H_5COOC_2H_5 + HSH.$$
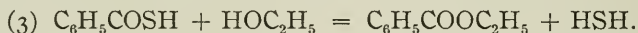
This has been verified by a study of the free acid and the reaction has been shown to be nonreversible.

Thiolbenzoic acid (23.5 grams) was dissolved in 12 cc., a slight excess, of absolute alcohol and hydrochloric acid was passed in. Though hydrogen sulphide begins at once to come off, the mixture was warmed for several hours to complete the reaction. After washing out the mineral acid with water, sodium carbonate was used to extract the remaining organic acid. This, on acidification, gave about a gram of benzoic acid and only a small drop of what may have been thiol acid. This shows that the reaction between thiolbenzoic acid and an equivalent amount of alcohol goes to completion instead of approaching a limit when about two-thirds of the thiol acid has reacted, as is the case with a mixture of benzoic acid and alcohol. The crude ester obtained gave, after drying, 18 grams of distillate between 212° and 215°, 3.5 grams from 215° to 219°, and about a gram above 219°, leaving a gram or so of solid residue. The fraction above 219° contained sulphur. The whole product was somewhat yellow. This experiment, though not all that might have been desired, shows clearly that the esterification of thiol-

[1] Wheeler: This Journal, **24,** 69.

[2] Cahours: Compt. Rend., **80,** 1317; **81,** 1163. Tüttscheff: N. Petersb. Acad. Bull., **5,** 395. Michler: Ann. Chem. (Liebig), **176,** 177. Willgerodt: Ber. d. chem. Ges., **18,** 328. Jones and Tasker: J. Chem. Soc., **95,** 1904.

[3] Z. Chem., **1868,** 353.

benzoic acid can be represented by equation (3), which is an abbreviation of (1′) above. There is no evidence that ethyl thionbenzoate is formed.

To test this reaction in the absence of any catalytic agent, the following experiments were made: Weighed quantities of thiolbenzoic acid and anhydrous alcohol were sealed up and heated for 68 hours to 145°–155°. The tubes were cooled in solid carbon dioxide and ether before being opened and then allowed to warm up very slowly. After the hydrogen sulphide had escaped, the tubes were emptied into water and the mixtures warmed to expel the rest of the hydrogen sulphide. They were then titrated with 0.1 N barium hydroxide, phenolphthalein being used as indicator.

The results are given in Table I. In the last four lines are given the weights of the acid and alcohol in grams and in millimoles, and in the last line the acid found, also expressed in millimoles.

Table I.

Weight of acid	0.5334	0.4509	0.4547	0.4932	0.5080
Weight of alcohol	0.2014	0.2084	0.1837	0.1710	0.1882
Acid (millimoles)	3.862	3.265	3.293	3.608	3.678
Alcohol (millimoles)	4.374	4.525	3.989	3.713	4.087
Acid found (millimoles)	0.351	0.147	0.093	0.276	0.202

Since some acid was found in each of these at the end, it might be concluded that the esterification was not complete. When, however, the combined neutral water solutions from all of these was evaporated to small volume and acidified, pure white crystals which contained no trace of thiolbenzoic acid were obtained. These were found to be pure benzoic acid. This shows that the thiolbenzoic acid had been completely esterified by heating with a slight excess of alcohol. Any water present in the thiolbenzoic acid would have decomposed some of the ethyl benzoate to form benzoic acid. The amount of water necessary to produce the largest amount of acid found is only 1.2 per cent. of the acid weighed in. Moreover, some of the benzoic acid was doubtless present as such in the beginning.

Ethyl Benzoate and Hydrogen Sulphide.

In order to test the reaction from the opposite direction, ethyl benzoate and hydrogen sulphide were heated together. The ester was weighed into a tube and saturated at —20° with the gas which had been passed over calcium chloride and then over phosphorus pentoxide. The tube was sealed, reweighed, and heated in the steel tube described below. The reaction mixture was titrated as before. The results are given in Table II, in the same form as above:

Table II.

	1.	2.	3.
Time (hours)	87	32	32
Temperature	170°	200–20°	200–20°
Ester (grams)	8.174	8.6796	10.2496
H₂S (grams)	1.173	0.4458	0.6189
Ester (millimoles)	56.2	57.83	69.89
H₂S (millimoles)	34.0	13.08	18.15
Acid found (millimoles)	0.348	4.462	2.852

The acid found in No. 1 was perfectly white and melted at 120°.5. In No. 2 the ester was extracted from the neutral solution left after the titration. Then the acid was extracted with ether after acidification, again titrated, and found to be 4.365 millimoles. The first titration may be slightly high owing to incomplete elimination of hydrogen sulphide from the reaction product, and the second may be low owing to incomplete extraction of the benzoic acid, but the fact that they are so near together shows that both of these errors are comparatively small. The acid was finally precipitated and proved to be pure benzoic acid. Thus it is shown that the reaction represented by equation (3) is not reversible and thiolbenzoic acid is not obtained by the action of hydrogen sulphide on ethyl benzoate.

Matsui[1] has found that water acts readily on ethyl thionbenzoate, $C_6H_5CSOC_2H_5$, eliminating hydrogen sulphide,

$$(4) \quad C_6H_5CSOC_2H_5 + H_2O \longrightarrow C_6H_5COOC_2H_5 + H_2S.$$
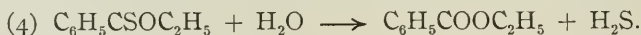
It was thought that this might be reversible and that the reaction product contained some thion ester and that this

[1] Mem. Coll. Sci. Eng., Kyoto, **1**, 285.

might react with the warm water used, during the titration, according to equation (4), so that what was being titrated was this hydrogen sulphide. The extraction of the acid and second titration was to test this. The results show that the acid found was benzoic acid and not hydrogen sulphide. Matsui showed that all thion esters react with alcoholic ammonia, even in the cold, with great ease, to form thioamides, hence the extracted ester was saturated at —20° with dry ammonia, sealed up, and heated to 60° for 24 hours. The reaction mixture was distilled with steam to get rid of the ester. A few milligrams of residue, which proved to be benzamide and not thiobenzamide, was obtained; this shows the absence of ethyl thionbenzoate and indicates the presence of some ethyl thiolbenzoate, since thiol esters give amides with ammonia at low temperatures while ethyl benzoate does not. The conclusion is then that hydrogen sulphide and ethyl benzoate react according to the following equation:

(5) $C_6H_5COOC_2H_5 + HSH = C_6H_5COOH + HSC_2H_5$.
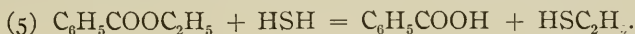
The resulting mercaptan would react, to a slight extent, with the benzoic acid to give ethyl thiolbenzoate and water. This is analogous to the action of potassium hydrosulphide on ethyl benzoate which I have shown to proceed according to the equation

(6) $C_6H_5COOC_2H_5 + KSH = C_6H_5COOK + HSC_2H_5$.
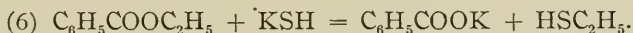
Schiff[1] found that ethyl acetate and potassium sulphide gave mercaptan.

The product in Experiment 3 was studied in a somewhat different manner but the same conclusions were arrived at.

Benzoic Acid and Ethyl Mercaptan.

Qualitative.—Benzoic acid (18 grams) and mercaptan (8 grams) were heated in a sealed tube. After cooling to —20°, and opening, the mercaptan remaining was distilled by gentle warming into a solution of lead acetate. Except for a trace of brown color where the delivery tube entered the solution, the precipitate had the pure yellow color of lead mercaptide, showing that no hydrogen sulphide was formed in

[1] Ann. Chem. (Liebig), **118**, 90.

the reaction. Water was also found and about a gram of liquid obtained boiling at about 245° (uncor.), which is far above the boiling point of ethyl benzoate and reasonably near that of ethyl thiolbenzoate. The other properties agreed with those of the thiol ester.

A similar experiment was tried with acetic acid and mercaptan and a small quantity of ester obtained which had the boiling point, 116°–117°, and the other properties of ethyl thiolacetate.

These experiments show that benzoic acid gives a clean reaction with mercaptan and that the products formed are those called for by equation (1″) or (4).

(7) $C_6H_5COOH + HSC_2H_5 \rightleftarrows C_6H_5COSC_2H_5 + HOH.$
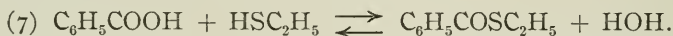
Quantitative.—Weighed amounts of benzoic acid and mercaptan and of ethyl thiolbenzoate and water were heated in small hard glass tubes of such size that they were rather more than half filled by the mixtures. Before use these tubes had been boiled six hours, or more, with dilute hydrochloric acid. The tubes containing the mixtures were enclosed in bits of thin brass tubing bearing numbers, and heated, a number at a time, in a large steel tube.

The Steel Tube.—This was a piece of heavy hydraulic tubing, 600 mm. long by 28 mm. inside diameter, with welded bottom and heavy screw cap and lead washer. It was jacketed with asbestos, clamped in an inclined position, and filled nearly full of kerosene. Temperatures up to 250° could easily be maintained by means of a Bunsen burner under the lower portion. The temperature was taken by a thermometer, the bulb of which dipped in a little pool of Wood's metal. Though the lead washer gave some trouble, this arrangement, as a whole, proved convenient and safe, since the external pressure on the glass tubes diminished their liability to explode and explosions of even large tubes, when they did occur, were perfectly harmless. Similar tubes have been used by others, but their use is not as general as it deserves to be.

After being heated, each tube was cooled in ice and salt and the capillary opened. A slight pressure was usually

found. The tube was then thrust, open end down, into recently boiled water which was still slightly warm. When the mercaptan had escaped, the tube was broken and the fragments placed in the water, which was then heated nearly to boiling in order to expel the rest of the mercaptan and to dissolve the benzoic acid. The acid present was titrated with 0.1 N barium hydroxide and phenolphthalein. There are several difficulties in the way of getting accurate results. Besides the usual trouble with carbon dioxide the mercaptan interferes with the indicator unless expelled by sufficient heating. The benzoic acid, being in a solid mass and saturated with the ester, dissolves with some difficulty unless considerable heat is applied, but benzoic acid escapes rapidly from hot solutions and hence much heating is to be avoided. The ethyl thiolbenzoate, like ethyl benzoate, is saponified with extreme ease, when suspended in hot water, by even a slight excess of alkali.

In Table III the results with mixtures of benzoic acid and mercaptan are given in the same form as above. The seventh line gives the amounts in millimoles of acid found at the end. These amounts are found by multiplying by ten the number of cc. of 0.1 N alkali required in the titrations. The amount of ester is found in each case by subtracting the final from the original amount of benzoic acid. The water formed is, of course, equivalent to the ester. The ester found is subtracted from the mercaptan taken to get the amount of mercaptan present at the end.

Since, according to the usual reasoning in the consideration of reversible reactions, the amount of ester found in unit time is equal to [*benzoic acid*][*mercaptan*] k, and the amount of ester decomposed in the same time equals [*water*][*ester*] k', (the expressions in brackets represent concentrations), and since at equilibrium these opposing velocities are equal, we have:

$$\frac{[\textit{benzoic acid}][\textit{mercaptan}]}{[\textit{water}][\textit{ester}]} = \frac{k'}{k} = r.$$

For equivalent concentrations of acid and mercaptan, at equilibrium,[1]

$$\frac{Amount\ of\ mixture\ unesterified}{Amount\ of\ mixture\ esterified} = \frac{\sqrt{k'}}{\sqrt{k}} = \frac{\sqrt{r}}{1}$$

Or,

$$\frac{Amount\ of\ mixture\ esterified}{1} = \frac{100}{\sqrt{r} - 1}$$

In percentages, this becomes

$$Per\ cent.\ of\ mixture\ esterified\ at\ limit = \frac{100}{\sqrt{r} - 1}$$

This value is given in the last line of the following tables.

Table III.—*Benzoic Acid and Mercaptan.*

Time in hours	42	70	70
Temperature	200–220°	200	200
Benzoic acid (grams)	0.3644	0.3621	0.3556
Mercaptan (grams)	0.2418	0.1881	0.2008
Acid (millimoles)	2.985	2.967	2.913
Mercaptan (millimoles)	3.893	3.028	3.233
Acid found at end (millimoles)	2.376	2.376	2.427
Ester = water	0.609	0.591	0.486
r	21.04	23.38	28.19
$\sqrt{r}$	4.587	4.835	5.310
Per cent. of ester	17.90	17.14	15.85

The average of these gives 16.86 as the percentage of esterification, at the limit, starting with a mixture of equivalent amounts of benzoic acid and mercaptan. Considering the difficulties mentioned above, the agreement in duplicate experiments is fair. One experiment was made in the same way with benzoic acid and alcohol, and 67.2 per cent. was found as the limit.

In Table IV are given the results of experiments with weighed quantities of ethyl thiolbenzoate and water. The data given correspond to those in Table III:

[1] Compare Bonz: Z. physik. Chem., **2**, 865.

Table IV.—Ethyl Thiolbenzoate and Water.

Time in hours	24	24	24	9	63
Temperature	210–20°	210–20°	210–20°	165–225°	200°
Ester (grams)	0.4740	0.5352	0.5142	0.5845	0.5080
Water (grams)	0.0732	0.0759	0.0787	0.0501	0.0755
Ester (millimoles)	2.853	3.221	3.095	3.518	3.058
Water (millimoles)	4.063	4.023	4.368	2.780	4.190
Acid found (millimoles)	2.571	2.868	2.803	2.533	2.847
Ester left (millimoles)	0.282	0.353	0.292	0.985	0.211
Water left (millimoles)	1.492	1.155	1.565	0.247	1.343
r	15.71	20.17	17.19	26.70	28.60
$\sqrt{r}$	3.964	4.492	4.146	5.167	5.347
Per cent. of ester at the limit	20.14	18.21	19.43	16.22	15.76

In several tubes which were heated to longer periods there was much decomposition, as shown by the dark color and by high pressure on opening. Such tubes give, on titration, low values for the benzoic acid present, which would give apparently high values for the amount of esterification. The high values may be due to slight decomposition, hence the mean of the three lower values, 16.73, is taken as the most likely value for the percentage of ester decomposed by an equivalent amount of water, at the limit. This agrees very well with the mean from Table III. From the value in the two tables, 16.8 per cent. may be taken as a final result.

Hence the reaction between benzoic acid and mercaptan obeys the mass law and a true equilibrium is reached with 16.8 per cent. esterification.

General Discussion.

The results of the experiments are just what would be expected according to Henry's hypothesis, though, of course, it is not concluded that they prove its correctness, since other equally good explanations may be found.

On the basis of this hypothesis it is shown that, in forming the intermediate addition product, mercaptan adds as H– and –SC$_2$H$_5$, and not as HS– and –C$_2$H$_5$. Alcohol may, or may not, act in an analogous manner, though the fact that mercaptan acts in this way favors the idea that alcohol does too.

Considering the intermediate compound postulated in equations (1′) and (2′), the fact that the thion ester,

$$C_6H_5CSOC_2H_5,$$

is not formed, indicates that from this complex hydrogen sulphide is more readily given off than is water, and the fact that the reaction represented by equation (3) is not reversible shows that hydrogen sulphide has little or no power to unite with ethyl benzoate to form such a complex. Matsui[1] has made ethyl thionbenzoate and has shown that it is decomposed by water with great ease. The reaction

$$(8)\ \ C_6H_5CSOC_2H_5 + H_2O = C_6H_5COOC_2H_5 + H_2S.$$
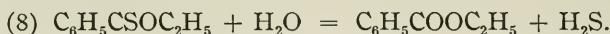
is not reversible. According to Henry's hypothesis, the same intermediate product would be postulated in this as in (1′) and (2′). These facts are then in thorough accord with each other and with what we know of hydrogen sulphide in organic chemistry. Energy changes must be the fundamental cause.[2]

If the reaction between benzoic acid and alcohol be written

$$(9)\ \ C_6H_5COOH + HOC_2H_5 \ \underset{1}{\overset{4}{\rightleftarrows}} \ C_6H_5COOC_2H_5 + H_2O,$$
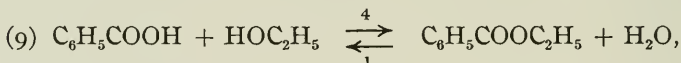
in which $\underset{1}{\overset{4}{\rightleftarrows}}$ is used to denote the fact that, for equivalent quantities, the reaction goes forward four times as fast as backwards, then the reaction between benzoic acid and mercaptan is to be written

$$(10)\ \ C_6H_5COOH + HSC_2H_5 \ \underset{25}{\overset{1}{\rightleftarrows}} \ C_6H_5COSC_2H_5 + H_2O.$$
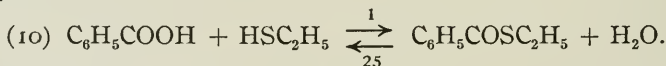
The intermediate product postulated in (1″) has a much greater tendency to split into mercaptan and acid than into thiol ester and water, while for the corresponding reaction between benzoic acid and alcohol, the intermediate compound splits more readily into water and ester than into acid and water.

Stating the facts in a somewhat different way, water is far more efficient in decomposing esters than is hydrogen sul-

[1] Mem. Col. Sci. Eng., Kyoto, **1**, 285.
[2] Compare Michael: THIS JOURNAL, **43**, 322.

phide. In reaction (9) the alcohol may be said to react four times as rapidly as water, while in (10) water appears to act 25 times as rapidly as mercaptan. It seems then that alcohol is 100 times as efficient in forming esters as its homologue, mercaptan.

Too much confidence must not be placed in this numerical comparison since the reactions take place in different media, etc., but emphasis is put on the fact, here brought out, that mercaptan esterifies acids to a far less extent and with, probably, a less velocity than does alcohol. It is an important observation that mercaptan, which, according to the periodic law, is the analogue of alcohol, really does behave like alcohol in esterification, one of the most important reactions of alcohol.

Zengelis[1] and Euler[2] suggested that esterification takes place according to the following process:

$$(11) \quad C_6H_5COOH + C_2H_5OH \underset{\longleftarrow}{\longrightarrow}$$
$$\overset{-}{C_6H_5COO} + \overset{+}{H} + \overset{+}{C_2H_5} + \overset{-}{OH} \underset{\longleftarrow}{\longrightarrow}$$
$$C_6H_5COOC_2H_5 + H_2O.$$
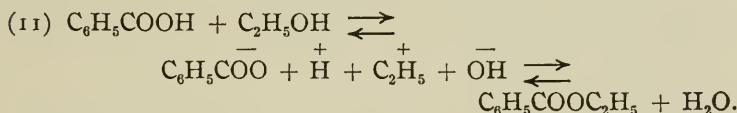
According to this, thiolbenzoic acid and alcohol should give a thiol ester, and benzoic acid and mercaptan should give an oxygen ester, which is exactly the reverse of what takes place.

Wegscheider[3] suggested that esterification proceeds as follows:

$$(12) \quad C_6H_5COOH + C_2H_5OH \underset{\longleftarrow}{\longrightarrow}$$
$$\overset{+}{C_6H_5CO} + \overset{-}{OH} + \overset{-}{C_2H_5O} + \overset{+}{H} \underset{\longleftarrow}{\longrightarrow}$$
$$C_6H_5COOC_2H_5 + H_2O.$$
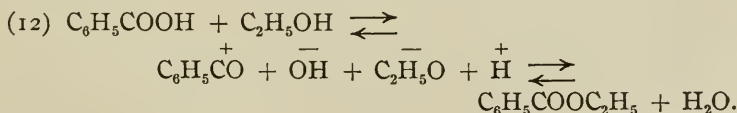
Euler[4] supposed that in saponification an ester breaks up into $C_6H_5CO—$ and $—OC_2H_5$. Wegscheider's supposition is in harmony with the facts here found relative to the esters formed, since according to it a thiol acid with alcohol should give an ester free from sulphur, but according to Euler's sup-

[1] Ber. d. chem. Ges., **34**, 198.
[2] Z. physik. Chem., **32**, 348.
[3] Monats. Chem., **16**, 75.
[4] Z. physik. Chem., **36**, 405.

position, thiolbenzoic acid and alcohol should give thiolben-
zoate which, in turn, should, with water, yield benzoic acid
and mercaptan.

In connection with V. Meyer's hindrance theory, Weg-
scheider[1] and Angeli[2] maintained that esterification of a silver
or other salt with an alkyl halide is replacement, but esterifica-
tion with an alcohol and hydrochloric acid involves addition
to the carbonyl group and is more likely to be "hindered" by
adjacent groups. This distinction is in harmony with the
fact that a salt of thiolbenzoic acid with ethyl bromide gives
a thiol ester,[3] while the free acid with alcohol yields an oxygen
ester. Wegscheider[4] found that a salt of hemipinic acid
gave with ethyl iodide an α ester, but the free acid with alco-
hol and hydrochloric acid gave a β ester.

Conclusions.

1. It is shown that the esterification of thiolbenzoic acid by
alcohol and of benzoic acid by mercaptan is in accordance
with Henry's hypothesis.

2. The reaction between benzoic acid and mercaptan is ex-
pressed by the equation

$$C_6H_5COOH + HSC_2H_5 \rightleftarrows C_6H_5COSC_2H_5 + H_2O.$$
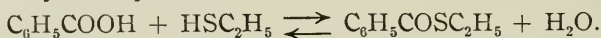
This reaction is reversible and the same equilibrium point
(about 17 per cent. of esterification with equivalent quantities)
is reached whether it proceeds from the one end or the other.

3. Mercaptan is shown to be the analogue of alcohol in its
power to esterify acids, both with and without a catalytic
agent. Mercaptan is, however, less efficient than alcohol.

The esterification of other acids by mercaptan is being
studied and esterification by other mercaptans will be taken
up. Since Tshugaey[5] has made selenomercaptan accessible, the
work may be extended to selenium compounds.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD., April, 1910.

[1] Ber. d. chem. Ges., **28**, 1468.
[2] *Ibid.*, **29**, Ref. 591.
[3] THIS JOURNAL, **24**, 69.
[4] Monats. Chem., **16**, 75.
[5] Ber. d. chem. Ges., **42**, 49.

ON THE SALTS OF TAUTOMERIC COMPOUNDS: REACTIONS OF URAZOLE SALTS WITH ALKYL HALIDES.

[SIXTEENTH COMMUNICATION ON URAZOLES.]

By R. F. BRUNEL AND S. F. ACREE.

(We are indebted to the Carnegie Institution of Washington for aid in our researches on tautomerism.)

This work[1] was undertaken to secure some *quantitative* data on tautomerism. Up to that time practically nothing but qualitative work had been done, with the result that especially Nef, Wheeler, Michael, Comstock, Knorr, and Wislicenus had developed theories to account for the interesting phenomena of such tautomeric compounds as quinazolines, amides, acetacetic ester, cyanides, cyanates, pyrazolones, uric acid derivatives, pyrimidines, rosanilines, phenolphthaleins, fluoresceins, etc. All of these theories had much to recommend them, and each one harmonized with most of the qualitative facts known at that time. It was perfectly clear, however, that since qualitative work by these brilliant colleagues for thirty years had not led to any one theory satisfactory to all chemists, further progress in tautomerism should be connected with an accurate *quantitative* investigation of the phenomena, a problem that would occupy a number of chemists for years even if they worked with but one class of substances.

Success in work on a problem depends as much upon the fortunate choice of substances and methods with which to secure *accurate experimental data* as upon the choice of really important points of attack, the solution of which will give us a deep insight into the complexity of the phenomena concerned. The senior author of this article has since 1896 been investigating the tautomeric phenomena of such amides as triazoles, urazoles, quinazolines, anilides, hydrazides, etc.,

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[1] Dr. Brunel's researches were carried out in 1904–6, and the following article is an abstract of his work as presented in 1906. The subject has since been investigated further but the essential conclusions derived from his work at that time remain unchanged to-day. See also THIS JOURNAL, **27**, 118; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1; **39**, 124, 226; **43**, 358. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909).

partly with the view of learning what class of substances would ultimately best lend themselves to the accurate study of the problem, and it seemed to us that the urazoles were of all these the ones best adapted to this end. It was all the more desirable to use urazoles and thiourazoles because they are cyclic derivatives of amides and thioamides, which had been the subject of so many beautiful investigations and speculations by Comstock, Wheeler, Nef, Michael, and others. We preferred to use the urazoles, especially 1-phenylurazole and its alkyl derivatives, for the following reasons: (1) This preliminary work had shown that the urazoles are fairly strong acids whose affinity constants can be measured, and which form stable salts not readily hydrolyzed or alcoholized and whose ionization constants in water, alcohol, etc., can therefore be readily measured; (2) we had shown by conductivity methods that these urazoles and their salts do not undergo *slow* tautomeric changes;[1] (3) the urazoles, and especially their salts, react readily at ordinary temperature with alkyl halides, acid chlorides, etc., and yield mixtures of *N*-alkyl (acyl) and *O*-alkyl (acyl) derivatives; (4) the derivatives obtained by alkylation, acylation, etc., seemed to be stable substances which could possibly be estimated quantitatively.

All of these properties of the urazoles seemed to make it possible to obtain, by means of them, some of the factors

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[1] In April, May and June, 1905, we carried out a large number of conductivity measurements with 1-phenyl-, 1-phenyl-2-methyl-, 1-phenyl-4-methyl-, 1-phenyl-3-thio-, and 1-phenyl-3-thio-4-methylurazole, and their salts, to determine their ionization constants and thus learn how far the ions and the molecular forms of the salts or acids are concerned in the alkylation, acylation, and other reactions. The salts, at dilutions of from 0.02 N to 0.00003 N, were treated with equivalent quantities of solutions of hydrochloric acid and the conductivities measured at different time intervals to ascertain whether there were slow changes of stronger tautomeric acids into weaker tautomeric acids, or *vice versa*. Taking into consideration changes of temperature on dilution, incomplete mixing, etc., the results showed that there were no appreciable variations in conductivity during even the shortest time periods; in other words, that any possible tautomeric changes take place too quickly to be followed by these methods, a conclusion also borne out by the constancy of the ratio *N*-ester : *O*-ester obtained from the salts and alkyl halides. Mr. E. K. Marshall has now, however, liberated some of these acids from their salts in alcohol at 0° and —70° *in the presence of diazo alkyls*, which react with great rapidity with these urazole acids, and has found that the acid so liberated may yield a ratio *N*-ester : *O*-ester which is different from that given by the acid if it is allowed to attain equilibrium by standing thirty minutes or longer. This work at low temperatures promises to be of great aid in attempts to ascertain whether tautomeric changes take place in some cases in which no such variations can be detected by other methods at present available.

necessary to the solution of our problem. We hoped afterwards to take up the quantitative study of those urazoles whose tautomeric forms and whose salts can be isolated and are found to change into each other slowly, and whose esters also rearrange.[1]

In order to secure the quantitative data necessary to the solution of this problem a large number of things must be investigated, among them:

1. What is the structure of the tautomeric acid or salt?[2] Are these urazoles and their salts amides, —CONH, or imides, —C(OH) = N—, or are they mixtures of two forms, some of which may be stable and others of which may change into each other? How may the constants involved in the equilibrium be affected by change in temperature, solvents, light, etc.? Does the equilibrium exist between molecules, or ions, or "residues"?

2. What is the mechanism of the reactions involved when the urazole or its salt, apparently a single substance, yields (*a*) one or (*b*) two classes of derivatives? Do the ions, or the molecules, or both, or complex groups, react in specific cases?

3. We have first taken up the study of the formation of the *N*-alkyl and *O*-alkyl (acyl, etc.) derivatives by the action of alkyl (acyl, etc.) halides, sulphates, nitrates, etc., on the urazoles and their salts. The following phases of these reactions were the first to be studied. (*a*) How does the velocity of formation of the *N*-ester and *O*-ester vary with changes in the alkyl halide, salt, solvent, temperature, illumination, electric or magnetic field, concentration, added salt, etc.? (*b*) Do *different salts* and the same alkyl halide give the same

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[1] This has now been done by Dr. Sidney Nirdlinger and Mr. E. P. Doetsch, (1907–1910) whose results will appear later. These colleagues have been able to show that 1,4-diphenyl-3-oxy-5-thionurazole and 1-4-diphenyl-3-oxy-5-thiolurazole, and their salts, rearrange into each other slowly enough to be studied. Each salt yields its own ester.

[2] Michael: (Ann. Chem.(Liebig), **363**, 20), divides tautomeric compounds into two classes: *desmotropic*, which change their structure reversibly through the movement of a hydrogen atom; and *merotropic*, which, though stable, yield derivatives of an isomer. I do not believe that we have *clear proof* that there is a single *merotropic* substance known to-day. Instead of begging this question we are trying to see whether those substances are not really *desmotropes which change into each very quickly*. Our urazoles, which, from some reactions, appear to be individuals, react at lower temperatures in other cases like mixtures. The subject needs much further work.

or different ratios of *N*-ester : *O*-ester under the same conditions? (*c*) Do *different alkyl halides* and the same salt yield the same or different ratios *N*-ester : *O*-ester under the same conditions? (*d*) Does the ratio *N*-ester : *O*-ester change with a variation in the temperature at which these esters are formed? (*e*) Does the ratio *N*-ester : *O*-ester change with the solvent in which the reaction takes place? (*f*) Does the ratio *N*-ester : *O*-ester change with the variation in the concentrations of the substances yielding these esters? (*g*) Does the ratio *N*-ester : *O*-ester change on the addition of a salt having a common cation with the salt yielding the ester, or upon the addition of other electrolytes or nonelectrolytes? Many other such questions have also suggested themselves.

It may be said now that when the theories of Comstock, Wheeler, Nef, and Michael are applied to our urazoles, the conclusions are not in harmony with the experimentally established facts. At the time these theories were proposed they were fine correlations of the known facts and have served beautifully as guides in the later work; they will be found to apply, without doubt, to many other, perhaps limiting, cases.

I. The Theory of Different Structures for the Potassium and Silver Salts of Tautomeric Compounds.

It has long been known that potassium cyanide with alkyl halides gives nitriles while silver cyanide gives isonitriles. The first attempt to explain this was made on the assumption that potassium cyanide is to be represented by the formula KCN, the silver salt by AgNC. In 1891, Comstock and Wheeler[1] noted a similar behavior on the part of the salts of formanilide and advanced the same theory to explain it. This explanation was, of course, based on the belief that the alkali salts give *only a N-derivative* and the silver salts *only an O-derivative*. Friedländer[2] obtained similar results with certain oxyquinazoline derivatives, and Wheeler[3] later made the *N*-alkyl and *O*-alkyl derivatives of *o*-aminophenoxyacetic anhydride from the potassium and silver salts. Comstock

[1] This Journal, **12**, 493 (1890).
[2] Ber. d. chem. Ges., **18**, 1529.
[3] This Journal, **20**, 555.

and Wheeler,[1] however, soon found that silver succinimide, when treated with an alkyl halide in the cold, gives some *N*-ester along with the *O*-ester. Both Claisen[2] and Michael,[3] moreover, had already found that sodium acetacetic ester gives with chlorcarbonic ester chiefly the *O*-derivative and a small amount of the *C*-derivative, whereas this salt and alkyl halides always give apparently only *C*-derivatives. Nef[4] later found that potassium cyanide always gives a mixture of nitrile and isonitrile, and silver cyanide sometimes gives both compounds. The mere assumption of one structure for the alkali salt, and another for the silver salt, is obviously insufficient to explain these reactions and has in fact long been abandoned by most writers. Sodium acetacetic ester gives with acetic anhydride[5] or with acid chlorides[6] a mixture of *O*- and *C*-derivatives and the copper salt behaves in similar manner. If the free ester is heated with silver oxide and an alkyl halide, a mixture of the *O*- and *C*-alkyl derivatives is obtained,[7] the former to the extent of about 5 per cent. The sodium salt[8] of acetylacetone, benzoylacetone, etc., gives with acid chlorides a mixture of the *O*-acyl and *C*-acyl derivatives, and the silver salt of acetylacetone or of diacetylacetic ester gives, when treated with ethyl iodide, a mixture of the *O*-ethyl and *C*-ethyl derivatives. Bogert[9] and Seil have published a fine review of the literature on analogous reactions of quinazolines, oxylepidines, etc., to which the reader is referred. The behavior of the potassium and silver salts of the urazoles, now worked out, is in complete accordance with these facts. Whichever salt we use, a mixture of *N*- and *O*-esters is obtained, although one may be formed in much greater amount; and furthermore, *in many cases, the*

[1] This Journal, **13**, 520 (1891).

[2] Ber. d. chem. Ges., **21**, 3397, 3567 (1888).

[3] J. prakt. Chem., [2] **37**, 473 (1887).

[4] Ann. Chem. (Liebig), **270**, 329 (1892).

[5] Ber. d. chem. Ges., **25**, 1046 (1892). Ann. Chem. (Liebig), **278**, 223 (1894).

[6] Ann. Chem. (Liebig), **277**, 182 and 199 (1893).

[7] J. Chem. Soc., **77**, 739 (1900).

[8] Claisen: Ber. d. chem. Ges., **25**, 1760. Nef: Ann. Chem. (Liebig), **276**, 232; **277**, 59; **287**, 269. Curtiss: This Journal, **17**, 435. Dieckmann: Ber. d. chem. Ges., **33**, 2002; **37**, 3370, 3384, 3392, 4627; **38**, 2977; **39**, 3052. Lapworth: J. Chem. Soc., **93**, 30.

[9] J. Am. Chem. Soc., **29**, 517; **31**, 507.

one present in smaller amount would easily have been missed if we had not looked for it. It is, therefore, not too much to say that it is probable that in the reactions of many, if not all, tautomeric compounds with reagents with which they could easily form two classes of derivatives—*O-* and *N-*, or *O-* and *C-*compounds, or others as the case may be—both are actually formed, *although the amount of one may be in many cases too small to be easily detected.* Comstock and Clapp[1] prepared a large number of *N-* and *O-*alkyl derivatives of anilides and toluides from the sodium and silver salts, respectively, and described the products obtained as pure, but, as far as their experimental data show, compounds of both classes could easily have been present in every case. Claisen[2] claims that sodium formanilide with ethyl iodide gives only a *N-*alkyl derivative, but the experimental data of the men[3] from whom he quotes do not justify this statement.

Another difficulty confronting those who advanced the above theory lies in explaining the formation of an *O-*silver salt from a *N-*sodium salt by the direct action of silver nitrate on the sodium salt in solution. But, as stated above, this theory has been largely given up, since it is of little, if any, assistance in explaining the phenomena of tautomerism. Not so, however, with the idea that the salts have a single definite structure, namely, that of the stronger of the two tautomeric acids, or of the enol form of amides, acetacetic ester, etc. That view is still held by the majority of workers in this field. The difficulty then arises in explaining the formation of two alkyl, acyl, etc., derivatives directly from a single salt, and the theories put forward in the attempt to explain these reactions will be taken up in the next two sections.

II. The Rearrangement Theory.

In most of the work referred to above not very much attention was paid to the effect that temperature or solvent may have on the products obtained. The ilver salts were generally

[1] This Journal, **14**, 525 (1892).
[2] Ann. Chem. (Liebig), **287**, 361 (1895).
[3] Ber. d. chem. Ges., **20**, 2273 (1887); **21**, 1106 (1888).

allowed to react[1] in the cold, usually in ether or benzene solution, while the alkali salts were as a rule heated in alcohol or mixtures of alcohol and water.[2] In 1899, Wheeler[3] attempted to prepare the *O*-ester of formanilide by heating the silver salt with ethyl iodide at 100° to save time. It had formerly been prepared from the silver salt in the cold. Wheeler obtained only the *N*-ester. He then investigated the behavior of a large number of imido esters when they were heated with alkyl halides,[4] and found that in nearly all cases they rearranged into *N*-esters. This beautiful work by Wheeler is of the very greatest importance in tautomerism, and must be considered in all alkylation, acylation, etc., reactions of tautomeric and other substances. He did not try to rearrange ethylphenylimido ester into the ethyl formanilide obtained above, but the reactions studied were exactly analogous. He therefore concluded that the *N*-alkyl esters in general are formed by rearrangement of *O*-esters first formed,

(1) $—N = C(ONa)— + CH_3I \longrightarrow$
$$—N = C(OCH_3)— + NaI.$$

(2) $—N = C(OCH_3)— + CH_3I \longrightarrow$
$$\begin{array}{c} —N——C(OCH_3)— \longrightarrow \\ \quad | \qquad | \\ \quad CH_3 \quad I \end{array}$$
$$—N(CH_3)CO— + CH_3I,$$
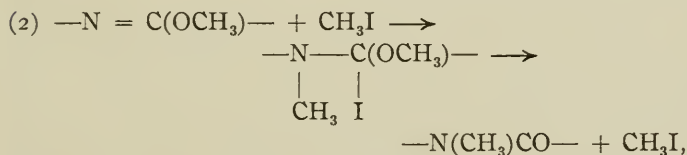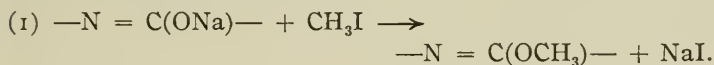
and made the following statement:[5]

"The tautomeric reaction in these cases, as in others, is undoubtedly nothing but one of addition." Although Wheeler held to the addition theory in general, the context shows that he here had in mind the addition of alkyl halide to an *O*-ester first formed and a subsequent rearrangement of that addition product into a *N*-ester and the alkyl halide. The same author later studied other rearrangements, taking up, among other compounds, the imido acid anhydrides; the following quota-

[1] This Journal, **13**, 525 (1891).
[2] *Ibid.*, **13**, 514.
[3] *Ibid.*, **21**, 185 (1899).
[4] *Ibid.*, **23**, 135 (1900); **21**, 185 (1898); **30**, 28.
[5] *Ibid.*, **21**, 187 (1899).

tion shows the conclusions reached:[1] "The results now at hand afford a satisfactory explanation for the behavior of sodium and silver salts of the amides and anilides with acid anhydrides and acyl chlorides...... In both cases imido-acyl anhydrides are formed as the first step of the reaction. Instead of the chloride acting by addition, as previously supposed, the acyl group directly replaces the metal. The products in the former case decompose at ordinary temperatures, while those in the latter rearrange into N-derivatives. *The action is similar to that of the alkyl halides, but the imido acid anhydrides undergo à molecular rearrangement with far greater ease than the imidoesters*" (italics ours). A similar view has been held by others. Claisen[2] found that the O-acetylacetacetic ester, when heated with potassium carbonate in ethyl acetate as solvent, was rearranged into the C-acetyl derivative, and that the reaction was accelerated by the presence of sodiumacetacetic ester. He concluded that this rearrangement furnished the explanation of the formation chiefly of the C-derivative in the acylation of the sodium salt by acetyl chloride.

Furthermore, a large number of O-esters of quinazolines,[3] α-quinolones,[4] pyridones,[5] antipyrines,[6] γ-oxyquinolines,[7] etc., rearrange *catalytically* into the N-esters when heated alone or with alkyl halides. In these cases Knorr, especially, showed that the catalytic action of the alkyl halide is due to the formation of an intermediate double compound (as in probably most cases of catalysis) between the O-ester and alkyl halide, which decomposes into the N-ester and the alkyl halide.

In none of these cases, however, is the evidence conclusive, although it certainly is convincing. The mere fact that rearrangement may take place is no proof that it alone is accountable for the formation of the two products. It was not proved in the above cases that the rearrangement takes place

[1] This Journal, **30**, 28 (1903).
[2] Ber. d. chem. Ges., **33**, 3778 (1900).
[3] Bogert and Seil: J. Am. Chem. Soc., **29**, 517.
[4] Knorr: Ber. d. chem. Ges., **30**, 929. Ann. Chem. (Liebig), **236**, 106; **293**, 1.
[5] Haitenger and Lieben: Monats. Chem., **6**, 322.
[6] Knorr: Ann. Chem. (Liebig), **293**, 1. Ber. d. chem. Ges., **30**, 922, 927, 929, 933.
[7] Knorr: Ber. d. chem. Ges., **30**, 937. Wenzel: Monats. Chem., **15**, 453.

rapidly enough to account for the amounts of the different compounds obtained. If these investigators had carried out the alkylation of silver formanilide and the rearrangement of ethyl phenylformimido ester under the same conditions of temperature, solvent, etc., and had studied the velocities of the reactions, it could then have been determined whether the amount of *N*-ester present was equal to that which should have been formed from the *O*-ester by rearrangement. Dieckmann[1] has criticized the above work of Claisen from this standpoint and in a preliminary paper has given results which indicate that the amount of *C*-acetyl derivative obtained by acetylation of sodium acetacetic ester is much greater than that obtained from the rearrangement of the *O*-acetyl body *under the same conditions*. It is necessary that experiments of this sort should be carried out quantitatively if the conclusions drawn from them are to be valid.

The results of our work on the urazoles show in two entirely different ways that the rearrangement hypothesis will not account for the phenomena here observed.

In all the alkylation experiments carried out quantitatively under varying conditions, from each salt a mixture of N- *and* O-*esters in practically a constant ratio was formed.*[2] The potassium salt of 1-phenyl-4-methylurazole was treated with one molecule of ethyl iodide in a mixture of ethyl alcohol-water at 25°, 60°, and 90°; the silver salt with one or two molecules of ethyl iodide in ether at 60° and 90°. In every case except in the experiment at 25° the reactions were complete in a few hours. If the *O*-ester rearranged into the *N*-ester the ratio of the amounts of these two esters would vary with the time; since no such variation was observed we can only conclude that the *O*-ester does not rearrange appreciably. All attempts to cause a rearrangement of the *O*- into the *N*-derivative, or *vice versa*, have, moreover, been unsuccessful.[3] The *O*-esters, heated with ethyl iodide

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[1] Ber. d. chem. Ges., **37**, 3392 (1904).

[2] Dr. J. M. Johnson has studied (1906–8) the alkylation of the potassium, sodium, barium, zinc, cadmium, mercury, cobalt, nickel, and other salts of 1-phenyl-4-methyl-urazole and obtained the same result.

[3] Dr. J. M. Johnson has now obtained evidence that the 1-phenyl-3-allyloxy-4-methylurazole can be changed at 100° into the corresponding 2-allyl derivative.

during 24 hours at 90° in alcohol and water, did not rearrange. In this case, however, the iodide was probably decomposed by the solvent in a few hours. To avoid this decomposition the experiment was repeated in ether and the temperature was kept at 200° for two hours; here again no rearrangement was detected. Furthermore, some of the alkylation experiments by Dr. J. M. Johnson, in which the O- or N-ester, urazole salt and alkyl halide were heated together under the conditions attending the alkylation experiments, furnish still more evidence on this point and show, as well, that the rearrangement does not take place in the opposite direction. They also answer the objection, which might be raised, that in the above experiments instituted to cause rearrangements the exact conditions existing during the alkylation were not reproduced. In some of the experiments with the silver salt, two molecules of the ethyl iodide were used. Some of the tubes, as the data show, were opened when the reaction had been under way only a short time while others were heated long after the alkylation process was complete. With the excess of ethyl iodide present there was every opportunity for rearrangement, yet the relative amounts of the two products was the same in all cases, within the limits of experimental error. The only way of reconciling these facts with the rearrangement theory would be to assume that the rearrangement reaction is instantaneously reversible, perhaps on account of some special catalytic action of some substance present. This possibility, which is very improbable in any case now known, would not harmonize with the fact that the ratio obtained from the potassium salt is greatly different from that yielded by the silver salt, and is disproved in Dr. J. M. Johnson's work by special experiments instituted to test this point by adding O-ester and N-ester to the alkylation mixture; the ratio of the amounts of these two esters was very close to that calculated on the assumption that no rearrangement takes place. If any rearrangement takes place in our experiments it is so small in amount that it cannot possibly account for the amounts of N-ester and O-ester obtained.

The Addition Theory.

Another theory used to-day as a correlation of the phenomena of tautomerism is the "addition theory" first proposed by Michael,[1] and since then upheld, at times, in the same general form by Nef[2] and others. Nef[3] has given up his views on this theory. According to Michael's conception the molecular form of the amide salts adds the alkyl halide and a mixture of the *N*-ester and *O*-ester is formed from this double compound. This theory looks very plausible when viewed from Michael's standpoint and when only qualitative facts are considered, but seems very improbable when all the *quantitative facts* known to-day are scrutinized.

Michael does not use the facts at the bottom of the ionization theory in connection with the "addition theory," but believes that the undissociated salts add the alkyl halide and that this double compound then yields the *N*-ester and *O*-ester. We have a large amount of experimental evidence showing that the *ions and the molecules* of the salt are both concerned in some of these reactions, and hence Michael's theory is weak in this respect.

The following examples, among many others, will suffice to show why we do not believe that Michael's theory can be a general correlation of the known facts. 1-Phenyl-3-thiourazole reacts readily with methyl odide and ethyl iodide when 0.05 N solutions of each are mixed at 50°. Now the hydriodic acid liberated in the reaction

$$\text{UrSH} + \text{ICH}_3 \longrightarrow \text{UrSCH}_3 + \text{HI}$$
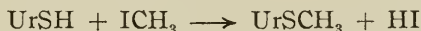
causes a suppression of the ionization of the fairly strong thiourazole acid ($K = 0.017$) and hence *a relative increase in the per cent. of the molecular form of the acid.* If, as Michael believes, only the molecular form of the acid reacts with the alkyl halide, *the reaction velocity should increase. As a matter of fact, the reaction velocity decreases very greatly, as is to be predicted from our theory, which will be discussed later.* The

[1] J. prakt. Chem., **37**, 469; **45**, 580; **46**, 189, and many later papers, especially This Journal, **43**, 322; Ber. d. chem. Ges., **43**, 621.
[2] Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83, etc.
[3] *Ibid.*, **298**, 263.

following table, worked out by Dr. G. H. Shadinger,[1] will illustrate this point:

0.05 Volume Normal[2] 1-Phenyl-3-thiourazole + 0.05 Volume Normal Ethyl Iodide in 50 Per Cent. Alcohol at 50°.
Shadinger.

$t.$ Min.	$A.$	$A-X.$	$X.$	$A_1K_1.$	$K_1.$
5	4.90	4.11	0.79	0.0392	1.568
10	4.90	3.57	1.53	0.0380	0.520
15	4.90	3.18	1.72	0.0367	1.468
31	4.90	2.46	2.44	0.0325	1.300
60	4.90	1.88	3.02	0.0273	1.096
120	4.90	1.29	3.61	0.0238	0.952

In the same way the addition of potassium iodide, for example (and other salts), should increase the per cent. of the molecular form of potassium (or other) urazoles in solution with alkyl halides and hence, if Michael's theory were correct, cause an increase in the reaction velocity. *As a matter of fact, in every case that we have studied, with one or two exceptions, the velocity is decreased to about the extent to be predicted from our theory.*[3]

Although a great many of Michael's ideas are very helpful in these problems, and he is without doubt one of our most brilliant organic chemists, is seems to us that the elemental weakness of his position is the failure to harmonize the facts of modern physical chemistry with his own ideas on the theory of organic reactions.

The Theory of Tautomeric Salts.

We took up this problem with the idea of securing evidence

[1] THIS JOURNAL, **39**, 271. Ber. d. chem. Ges., **41**, 3234.

[2] The values A_1K_1 and K_1 are calculated on the normal basis; *i. e.*, on the basis that A is 5.00 instead of 4.90 (*loc. cit.*).

[3] A large number of other weak points in Michael's theory will be discussed soon in an answer to his recent criticism of our urazole work (THIS JOURNAL. **43**, 322. Ber. d. chem. Ges., **43**, 621). Mr. H. C. Robertson has now shown by measuring the ionization of sodium phenolate and its velocity of reaction with methyl iodide and ethyl iodide in absolute alcohol, that the phenolate ions react about 7 times as rapidly as the sodium phenolate molecules (or, what is kinetically equivalent, the sodium ions and the phenolate ions together). Mr. S. K. Loy has shown the ethylate ions and sodium ethylate molecules (*vide* preceding parenthesis) to react with about the same velocities with methyl iodide.

on the three theories already discussed and on the theory of tautomeric salts. It seemed possible that both the imide and the enol group of the two tautomeric forms, (I) and (II), of 1-phenyl-4-methylurazole could give salts which should react with alkyl halides. Such imide salts as potassium[1] pyrrole and alkali

$$C_6H_5N — NH \qquad C_6H_5N — N$$
$$O:C \quad CO \quad \rightleftharpoons \quad O:C \quad COH$$
$$NCH_3 \qquad\qquad NCH_3$$
$$\text{I.} \qquad\qquad\qquad \text{II.}$$

$$C_6H_5N — NNa \qquad C_6H_5N — N$$
$$O:C \quad CO \quad \rightleftharpoons \quad O:C \quad CONa$$
$$NCH_3 \qquad\qquad NCH_3$$
$$\text{III.} \qquad\qquad\qquad \text{IV.}$$
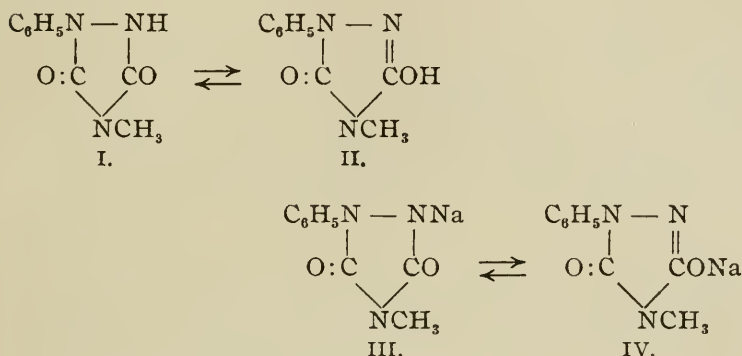
salts of aniline[2] and diphenylamine act readily, violently in some cases, with alkyl halides, and the pyrrole salts also react with acid chlorides.[3] The enol salts should react with alkyl halides in a manner analogous to the formation of esters from the sodium salts of organic acids and alkyl halides. *It seemed possible then that in all cases in which these tautomeric urazoles give two or more stable isomeric products as the result of a reaction they do so because they exist in two or more tautomeric forms in equilibrium, each of which reacts independently, or because one form is changed into stable derivatives through two or more side reactions.*

If there are two salts whose molecules are in equilibrium, the reaction may be expressed graphically[4] as follows:

[1] Ber. d. chem. Ges., **17**, 2951.
[2] *Ibid.*, **6**, 1514.
[3] *Ibid.*, **18**, 881.
[4] *Ibid.*, **41**, 3199.

$$C_6H_5N - NNa$$
$$O:C \quad CO \overset{K_1}{\rightleftarrows} O:C \quad CO + \overset{+}{Na} + CH_3I \longrightarrow$$
$$NCH_3$$

$$C_6H_5N - \overline{N}$$
$$O:C \quad CO + \overset{+}{Na} + CH_3I \longrightarrow$$
$$NCH_3 \quad C_6H_5N - NCH_3$$
$$O:C \quad CO + NaI$$
$$NCH_3$$

$$C_6H_5N - N$$
$$O:C \quad CONa \rightleftarrows O:C \quad \overset{-}{CO} + \overset{+}{Na} + CH_3I \longrightarrow$$
$$NCH_3 \qquad NCH_3 \quad C_6H_5N - N$$
$$O:C \quad COCH_3 + NaI$$
$$NCH_3$$
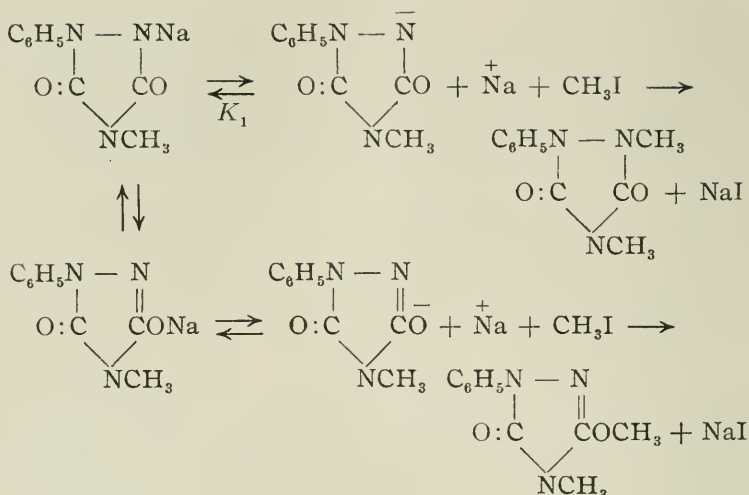
Let the concentration of the total urazole salt be represented by $C_{urazole\ salt}$, that of the alkyl halide by $C_{alkyl\ halide}$, that of the undissociated keto salt by C_{km}, that of the keto ions by C_{ki}, that of the undissociated enol salt by C_{em}, and that of the enol ions by C_{ei}, and assume that the value of K_3 in the equation $K_3 = \dfrac{C_{km}}{C_{em}}$ remains practically constant during the reaction. Let x be the concentration of N-ester and x_1 that of the O-ester formed in the time t. Then the following equations must hold:

$$\frac{dx}{dt} = k_{1trans}(C_{urazole\ salt} - x - x')(C_{alkyl\ halide} - x - x') \quad (1)$$

$$\frac{dx'}{dt} = k_1'_{trans}(C_{urazole\ salt} - x - x')(C_{alkyl\ halide} - x - x') \quad (2)$$

$$\frac{d(x + x')}{dt} =$$
$$(k_{1trans} + k_1'_{trans})(C_{urazole\ salt} - x - x')(C_{alkyl\ halide} - x - x') \quad (3)$$

$$\frac{k_{1trans}}{k_1'_{trans}} = \frac{x}{x'} = \frac{N - ester}{O - ester} \quad \dots \dots \dots \dots \dots \dots \dots \quad (4)$$

It makes no difference whether the undissociated salt, or the ionized portion, or both, are reacting with the alkyl halide; the equations still hold and we then have $K_{1_{trans}} = K_{mol} \, C_{km} + K_{ion} C_{ki}$ and $K_1{}'_{trans} = K'_{mol} C_{em} + K'_{ion} C_{ei}$. These equations are based on the assumption that Arrhenius' ionization theory holds more accurately than our experimental data.

(1) This theory of tautomeric salts then leads us to the conclusion that the total ester, N-ester + O-ester, as well as the N-ester and the O-ester, individually, must be formed with a velocity expressed by a reaction of the second order. This we have found to be true for the potassium salt (page 545), and Dr. J. M. Johnson has shown it to hold for a number of other salts.

(2) According to these equations the ratio N-ester : O-ester should be a constant throughout the reaction. This has been found true of both the potassium and the silver salts, as can be seen on page 546, 547.

(3) If the values of K_{mol}, K'_{mol}, K_{ion}, K'_{ion}, $C_{ei} : C_{em}$, and $C_{ki} : C_{km}$, vary with different salts, then different ratios of N-ester : O-ester might be obtained from different salts. We have found this to be true of the potassium and silver salts, and Dr. J. M. Johnson showed the same for a large number of other salts. The ratio N-ester : O-ester for the potassium salt is about 91 : 9 at 60° in 40 per cent. alcoholic solution, and about 38 : 62 for the silver salt at 60° in ether.

The work presented in this paper does not give absolute evidence on the question whether the ions or the undissociated salts react with the alkyl halides but observations recently made by Dr. F. M. Rogers (1908), Mr. H. C. Robertson (1909–1910), and Mr. S. K. Loy (1909–1910), in this laboratory show that both ions and molecules are reacting in certain cases. When both ions and molecules are appreciably concerned in the reactions we may find corresponding variations in the ratios of esters, reaction velocities, and changes in concentration. All the facts presented in this paper are in harmony with the idea of two tautomeric salts in instantaneous equilibrium, and, taken in connection with our recent work, give

very strong evidence in favor of this view. The entire question will be discussed fully in a subsequent article.

At the outset of this work a study of the alkylation of potassium phenylurazole by various alkyl iodides was made and by this means a number of derivatives with radicals at position 2 were prepared. In former work it had been noted that the products from the action of alkyl iodides on the potassium and silver salts were never pure, and Acree had already suspected that alkylation took place at more than one position. Our first aim was to see if there was evidence that some *O*-ester was also formed from the potassium salt along with the main product—the *N*-ester. It was also thought possible that some of the higher alkyl derivatives would have such solubilities that they would be easier to separate and purify than the methyl and ethyl compounds, and that our investigation could thus be made much easier. In most cases it was proved that some *O*-derivative was present, but in these experiments we could not isolate the compounds in pure enough condition to determine exactly how much, and it is quite possible that in the cases where no evidence of its presence was found it was missed by some error in manipulation. It was also discovered later that the reaction mixtures were heated much longer than was necessary and that the excess of alkali used in some cases produced a partial decomposition of the compounds—probably a breaking open of the urazole ring. In the case of the isobutyl and isoamyl compounds only a trace of *O*-derivatives was detected. In the other cases, the amount appeared to be from 10 to 20 per cent. of the total alkylated product.

The melting points of these compounds as given below are of some interest. It is to be noted that if we except the methyl derivative, which generally melts higher than the corresponding ethyl derivative, the melting points of the urazoles having substituting groups with normal carbon chains increase as the weight of the radical increases, while the melting points of branching chain derivatives decrease with increase in weight of the substituting radical:

1-Phenyl-2-methylurazole, 184°–185°.
1-Phenyl-2-ethylurazole, 119°.5.
1-Phenyl-2-*n*-propylurazole, 128°.5.
1-Phenyl-2-*n*-butylurazole, 130°.
1-Phenyl-2-isopropylurazole, 161°.5.
1-Phenyl-2-isobutylurazole, 153°.
1-Phenyl-2-isoamylurazole, 97°.

Much more accurate analytical results were obtained in the alkylation of the salts of 1-phenyl-4-methylurazole. The method is liable to an error of two or three per cent. but, considering the difficulty naturally attending the quantitative separation of organic compounds having about the same solubilities, it is very satisfactory and will be shown to be accurate enough to justify the conclusions drawn. In the alkylation of potassium 3-thiourazole the results are still more accurate as the course of the reaction can here be followed by titration methods.

EXPERIMENTAL.

Phenylurazole.—Phenylurazole was prepared according to the method described by Acree.[1] It melts at 261°–262° and is practically insoluble in benzene, ligroin, carbon tetrachloride and chloroform as was determined in the following manner: Five-tenths of a gram of substance was allowed to stand with 10–12 cc. of each solvent for twenty-four hours at room temperature, being shaken at intervals. The solution was then filtered into a weighed porcelain dish and quickly weighed. After evaporation of the solvent the residue was weighed.

	Benzene.	Ligroin.	Carbon tetrachloride.	Chloroform.
Wt. solution	9.11	6.25	11.91	13.91
Wt. residue	0.0015	0.00	0.0005	0.00

The solubility in benzene, which is the greatest, is thus less than one part in five thousand.

Phenylurazole is acid to phenolphthalein, which was used in all titrations unless otherwise specified. The alkali used was in all cases potassium hydroxide.

[1] This Journal, **27**, 126 (1902).

1-Phenyl-2-methylurazole.—This had already been prepared by Acree[1] by the action of methyl iodide on potassium phenylurazole. A product melting at 185° was obtained by this method. It was also prepared by dissolving potassium phenylurazole in water and shaking with an excess of dimethyl sulphate. The alkylated product gradually separated out and was filtered off. It was separated from phenylurazole by extraction with chloroform. It melted at 183° and, after one crystallization from water, the melting point was 185°–186° and this was not changed on mixing the substance with that obtained by use of methyl iodide. Analysis:

0.1241 gram substance gave 24.5 cc. nitrogen at 25°.8 and 764.9 mm.

	Calculated for $C_9H_9O_2N_3$.	Found.
N	22.03	22.22

In the following alkylation experiments we expected to obtain:

(1) Unchanged phenylurazole, because the hydriodic acid, from the hydrolysis of the alkyl iodide, would liberate phenylurazole from the salt.

(2) 2-*N*- and 3-*O*-alkyl derivatives.

(3) Traces of 5-*O*- and of 4-*N*-alkyl derivatives which it would have been so difficult to separate from the 2-*N*-compounds that this was not attempted; and

(4) The various possible dialkylated products.

The general method of isolating these products was to evaporate the solution to small bulk at the end of the experiment, filter off the substance which separated out, and extract it, when dried, with chloroform. This left undissolved any regenerated phenylurazole, together with inorganic substances, but dissolved all of the alkylated products. The chloroform was evaporated and the residue was then taken up in alkaline solution, in which the monoalkyl derivatives are soluble; any insoluble dialkylated products were extracted by ether or chloroform.

The monalkyl derivatives were then precipitated by acidi-

[1] This Journal, **27**, 128 (1902).

fying the alkaline solution, filtered off and evaporated to dryness several times with concentrated aqueous hydrochloric acid and sufficient alcohol to bring them into solution, in order to convert into phenylurazole any *O*-alkylurazole present. A second extraction with chloroform then left behind any phenylurazole so formed. Evaporation of the chloroform solution should then give only 2-*N*- together with a little 4-*N*-alkyl derivative and some impurities. The main product was obtained pure by repeated recrystallization, precipitation from alkaline solution, etc., as described below.

1-Phenyl-2-ethylurazole.—Five grams of phenylurazole in 35 cc. alcohol were titrated with 0.9 N potassium hydroxide (about 30 cc.); 5.6 grams (1.25 molecules) ethyl iodide were added and the solution was made up to 100 cc. with alcohol. This was heated 4.5 hours on the water bath under a return condenser. About one-third of the solvent was then evaporated off and, on cooling, 0.8 gram phenylurazole, melting at 262°, crystallized out. Ethyl iodide is decomposed by water and gives hydrogen iodide; this would account for the liberation of phenylurazole. The solution was evaporated to about 15 cc. and an oil separated out, which solidified when cooled and rubbed. This was recrystallized from hot alcohol, the iodine being removed by thiosulphate. Its melting point was not sharp, about 88°. Extraction with chloroform left 0.2 gram substance melting at 235° (impure phenylurazole), while evaporation of the chlorform solution gave 3.5 grams substance melting at 101°, still not sharply. For the neutralization of 0.1023 gram of this product 5.34 cc. 0.907 N alkali, instead of the calculated 5.50 cc., were required. The main portion was then evaporated twice to dryness in an open dish with alcoholic hydrochloric acid in order to convert any ethoxy body present into phenylurazole. Extraction with chloroform then left 0.4 gram phenylurazole melting at 262°, and evaporation of the chloroform gave a substance melting at 110°–116°. This was extracted four times with the same lot of water (50–75 cc.) at 50° and allowed to crystallize each time at 0°. The fractions so obtained melted at 117°.5, 118°, 119°, 119°, respectively, but all softened at about 115°. The

whole amount, weighing 0.2106 gram, was titrated with 0.907 N alkali. Calculated, 11.32; required, 11.12 cc.

The substance was then precipitated in two fractions by sulphuric acid. The second fraction was purer. It softened at 117° and melted at 118°.5–119°. These last two lots weighed together 1.7 grams. On evaporation of the acidified solution to a small bulk crystals melting at 80°, but in too small amount for identification, separated out.

Five grams of phenylurazole thus gave 1.0 gram unchanged material, 3.5 grams alkylated product, 0.5 gram ethoxy derivative, and 2.1 grams pure 2-*N*-ester, melting at 119°. Analysis: 0.1246 gram substance gave 22.95 cc. nitrogen at 25°.8 and 765 mm.

	Calculated for $C_{10}H_{11}O_2N_3$.	Found.
N	20.53	20.73

This ethyl derivative is easily soluble in ether, chloroform, hot alcohol and hot water; difficultly soluble in cold water or alcohol.

Silver Salt.—About 0.3 gram substance was titrated with alkali; and then one equivalent of 0.1 N silver nitrate solution was added. The precipitate formed redissolved until about one-half the required amount of silver nitrate had been added, then became permanent. This phenomenon has been observed in many other cases in our urazole work, and indicates that a *soluble* alkali-silver double salt is present in solution. The solution was boiled, then cooled, and the salt was filtered off. Dried at 100°, it darkened very slightly and then melted at 259°, apparently with little decomposition. Analysis:

0.1143 gram substance gave 0.0399 gram silver.

	Calculated for $C_{10}H_{10}O_2N_3Ag$.	Found.
Ag	34.58	34.97

*1-Phenyl-2-*n-*propylurazole.*—To 5 grams phenylurazole, neutralized with alkali, were added 20 cc. alcohol and 6 grams (1.25 mols.) *n*-propyl iodide. The solution was heated to boiling under a return condenser for eleven hours, then the

product worked up as in the case of the 2-*N*-ethyl derivative described above. After hydrolysis of the *O*-esters present and removal of the phenylurazole so formed, a small amount of substance insoluble in alkali was found. The alkaline solution was extracted twice with ether and evaporation of this ether solution gave a small amount of oil, perhaps di-*N*-ester. The alkaline solution was acidified fractionally and gave four lots of propyl derivative varying in melting point from 127° to 128°.5. The whole amount was recrystallized from 50 per cent. alcohol and 2.4 grams, melting at 128°, were obtained.

Five grams of phenylurazole thus gave 0.4 gram regenerated diphenylurazole, 5.3 grams crude alkylated product, 0.86 gram *O*-ester, a trace of 2,4-di-*N*-ester, and 2.4 grams pure *N*-ester, melting at 128°. Analysis:

0.1205 gram substance gave 20.2 cc. nitrogen at 27°.5 and 762 mm.

	Calculated for $C_{11}H_{13}O_2N_3$.	Found.
N	19.27	18.63

Silver Salt.—Two lots of this salt were prepared by the same procedure described for the ethyl derivative. In the first case two drops of alcoholic phenolphthalein were used for the alkali titration and the silver salt turned dark before filtration. The experiment was repeated and solid phenolphthalein was used. The melting points of the two specimens were not sharp and did not agree, being 132° and 150°. Both, however, gave fairly good analyses:

I. 0.1049 gram substance gave 0.0348 gram silver.

II. 0.1754 gram substance gave 0.0577 gram silver.

	Calculated for $C_{11}H_{12}O_2N_3Ag$.	Found.	
		I.	II.
Ag	33.10	33.27	32.90

*1-Phenyl-2-*n-*butylurazole.*—Five grams of phenylurazole were titrated with alkali and 10 cc. alcohol and 6 grams (0.5 mols.) *n*-butyl iodide added. This solution was heated to boiling for ten hours under a return condenser. Ten cc. more alcohol were added and the heating was continued twenty

hours longer. The procedure was practically the same as for the ethyl and propyl derivatives. The final product was dissolved in alkali and precipitated in five fractions. These melted at about the same point, the first two sharply at 130°, while the others softened at 125°.5. The melting point is very close to that of the propyl derivative above (128°), but a mixture of the two melted at 123°.

Five grams of phenylurazole, then, gave 0.9 gram unchanged substance, 3.1 grams crude product, 0.35 gram *O*-ester, a trace of 2,4–dialkyl derivative, and 1.3 grams pure 2-*N*-ester, melting at 130°. Analysis:

0.1304 gram substance gave 21.1 cc. nitrogen at 27°.5 and 762 mm.

	Calculated for $C_{12}H_{15}O_2N_3$.	Found.
N	18.06	18.00

1-Phenyl-2-isopropylurazole.—Five grams of phenylurazole were neutralized with alkali, 6.2 grams (1.25 mols.) isopropyl iodide and 10 cc. alcohol were added, and the mixture was heated to boiling for five hours. The treatment of the product was the same as in the above cases. The product finally obtained melted at 161°.5, softening at 160°. An attempt was made to prepare a silver salt, but it came down in such gelatinous condition that it could not be separated out pure.

Five grams of phenylurazole, then, gave 2.2 grams unchanged phenylurazole, 2.5 grams crude product, 0.69 gram *O*-ester, and 0.75 gram *N*-ester. Some was lost. After the hydrolysis with acid a trace of product insoluble in alkali—di-*N*-alkyl derivative—was present. The *N*-ester melted at 161°.5.

1-Phenyl-2-isobutylurazole.—Five grams phenylurazole were neutralized with alkali. To this were added 6 grams isobutyl iodide and 30 cc. alcohol, and the mixture was heated to boiling under a return condenser twenty-eight hours. The procedure was the same as in the preceding cases.

Five grams substance gave 2.5 grams unchanged phenylurazole, a trace of *O*-ester, a trace of di-*N*-derivative, and 1.2 grams pure 2-*N*-ester, melting at 152°.5, first softening at 149°. Analysis:

o.1301 gram substance gave 21.35 cc. nitrogen at 27°.5 and 762 mm.

	Calculated for $C_{12}H_{15}O_2N_3$.	Found.
N	18.06	18.24

Silver Salt.—1-Phenyl-2-isobutylurazole, weighing 0.3147 gram, was titrated with 0.101 N alkali, 13.52 cc. being required instead of the calculated 13.37 cc. One molecule of silver nitrate was added and the solution was boiled to make the precipitate filter more readily. No definite melting point could be obtained. The salt contained too large a percentage of silver. Analysis:

 I. 0.1531 gram substance gave 0.0499 gram silver.

 II. 0.1812 gram substance gave 0.0542 gram silver.

	Calculated for $C_{12}H_{14}O_2N_3Ag$.	Found. I.	II.
Ag	31.73	32.59	33.68

1-Phenyl-2-isoamylurazole.—Five grams phenylurazole were titrated with alkali, 10 cc. alcohol and 7 grams isoamyl iodide were added, and the whole was boiled twenty-one hours. The procedure was the same as above. The total yield of pure 2-N-isoamylurazole melting at 97°–98° was 1.5 grams. Under water the substance became liquid at 75°. In every case it separated from the solvent —chloroform or alcohol— as an oil which solidified on cooling.

Five grams phenylurazole gave 4.1 grams crude product, 0.3 grams unchanged phenylurazole, a slight amount of O-ester and of the 2,4-di-N-ester, and 1.5 grams pure 2-N-isoamyl derivative, melting at 97°–98°. Analysis:

o.1429 gram substance gave 21.62 cc. nitrogen at 26°.5 and 761 mm.

	Calculated for $C_{13}H_{17}O_2N_3$.	Found.
N	17.04	16.86

Experiments described below indicate that these reactions were in every case complete in a few hours, so that the long heating was superfluous. The 2-alkyl derivatives obtained above are all easily soluble in chloroform and benzene, diffi-

cultly in water, more readily in alcohol. These solubilities all appear to decrease slightly with increase in the weight of the alkyl groups. In every case some 3-*O*-alkyl derivative was formed, but the amounts found should not be taken as exact since a quantitative method of separating the products had not then been worked out. In nearly every case some material insoluble in alkali was present, but the quantity was never sufficient for investigation. Later experiments, however, have shown that the 2-ethyl-4-methyl compound, at least, is volatile on the water bath, so that the amount of dialkyl product formed in any case may have been greater than the results indicate.

Action of Ethylene Dibromide.—Five grams of phenylurazole were neutralized with alkali and heated with two molecules of ethylene dibromide in 40 per cent. alcohol for twenty hours. Considerable phenylurazole was recovered and a gum was also obtained which was soluble in ether and hot alcohol, somewhat soluble in hot water, and which gave, with copper oxide, a strong test for bromine. It was too impure and the amount was too small for further investigation. It was found that the flame test for bromine with copper oxide must be used with caution, since phenylurazole[1] gives a slight greenish color.

1-Phenyl-2,4-diethylurazole.—Five grams of phenylurazole were dissolved in th ee equivalents (about 85 cc.) of potassium hydroxide solution. To the solution three molecules (13.2 grams) ethyl iodide and 21 cc. alcohol were added. After boiling for eighteen hours the solution was nearly neutral, so one-half molecule more alkali was added and the boiling continued eighteen hours longer. The solution was then evaporated to dryness, a small amount of water was added, the solution made alkaline, and the insoluble oil, which appeared, separated by extracting five times with ether. Chloroform would have been better for this purpose.

The alkaline solution gave, on acidification, 2.5 grams of 1-phenyl-2-ethylurazole melting fairly sharply at 119°. Ex-

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[1] Hugo Milrath (Chem. Ztg., **33**, 1249; Chem. Abs., **4**, 907) has recently called attention to the fact that other nitrogen compounds behave in this way. The Beilstein test for halogens should not be used in these cases, a direct method being preferable.

traction of this material with chloroform left only inorganic matter. After evaporation with hydrochloric acid no regenerated phenylurazole was obtained, but the material after one recrystallization from alcohol melted sharply at 119°–119°.5. When mixed with 1-phenyl-2-ethylurazole melting at 119°, the melting point was unchanged.

Evaporation of the ether solution above gave an oil. This was evaporated several times with alcohol and hydrochloric acid, and the product extracted repeatedly with ether. This took up the oil and left no phenylurazole. The material at this point was a somewhat yellowish oil, soluble with some difficulty in ether, which would not solidify on being rubbed with ligroin. It was apparently, as would be expected, the 1-phenyl-2,4-diethylurazole. The fact that, although the phenylurazole was apparently completely alkylated, only 2–3 grams of product was obtained is due to decomposition of the compounds by the excess of alkali used. It is shown below that the 2-ethyl-4-methyl compound is decomposed to a considerable extent by standing at room temperature for twenty-four hours with a moderate excess of alkali. This fact accounts also for the poor yields in the attempts to prepare various 4-alkyl derivatives, in which an excess of alkali was always used. Analysis of the oil:

0.2205 gram substance gave 36.0 cc. nitrogen at 21°.5 and 750 mm.

	Calculated for $C_{12}H_{15}O_2N_3$.	Found.
N	18.06	18.38

Alkylation in Absolute Alcohol.—Five grams of potassium phenylurazole were heated to boiling in absolute alcohol with 1.5 molecules ethyl iodide for eleven hours. The salt is only moderately soluble in alcohol. The material that first separated out was phenylurazole with 15–20 per cent. of alkylated product, but the melting point was only 10°–12° lower than that of pure phenylurazole, although not at all sharp. No indication of the presence of any 3-ethoxy derivative was obtained. A product was isolated which melted at 116°, but when this was mixed with the 2-ethyl derivative melting

at 119° the mixture melted at 105°. Another product weighing less than 0.1 gram and melting at 84° was also isolated. The quantity of each of these was too small for further purification. The former may have been a mixture of the 2- and 4-ethyl derivatives.

Ethyl Carbethoxythioncarbamate.—This was prepared according to the method of Delitsch[1] and Wheeler.[2] The yield was poor in all cases. An attempt was made to purify the product by distillation in a vacuum, but at 20 mm. pressure only 2.5 grams of pure substance were obtained by distillation of 25 cc. of the oil, showing that decomposition must have taken place during the distillation. In one case it was attempted to isolate the product by pouring the reaction mixture directly into an alcoholic solution of 1.5 molecules of potassium hydroxide, but the yield of the thion compound, in that experiment, from 150 grams of ethyl chlorcarbonate, was only 30–40 grams. The best yield obtained was 85 grams from 100 grams of the chlorcarbonic ester, or about 50 per cent.

1-Phenyl-3-ethoxyurazole.—This was prepared by the method of Wheeler,[3] who heated the carbethoxythioncarbamic ester with phenylhydrazine. The process should be carried out in an atmosphere of carbon dioxide to avoid, as far as possible, the formation of a deep red compound rather difficult to remove. This colored substance is difficultly, if at all, soluble in ether, somewhat more so in benzene; but it can best be removed by extracting the dry 1-phenyl-3-ethoxyurazole salt with alcohol. The ethoxy body obtained melted at 149°–150°. The melting point formerly obtained was 152°.[4]

1-Phenyl-3-ethoxy-4-methylurazole.—This was prepared by dissolving the ethoxy compound in a small excess of alkali and shaking the solution with somewhat of an excess of dimethyl sulphate. The water and alkali decompose the dimethyl sulphate, and 1-phenyl-3-ethoxyurazole is liberated, so that frequent addition of more dimethyl sulphate and alkali is

[1] J. prakt. Chem., [2] **10**, 118 (1874).
[2] J. Am. Chem. Soc., **22**, 377 (1900).
[3] *Loc. cit.*
[4] Ber. d. chem. Ges., **36**, 3146 (1903).

necessary. The alkylation product separates out and is filtered off. The melting point, without further purification, was 93°, that found formerly being 95°.[1] The yield was, however, only about 75 per cent. of the calculated, probably on account of decomposition of the material by the excess of alkali. This danger was not discovered until later in the work. Dr. J. M. Johnson has found that better yields are obtained if the solution of the urazole salt is heated to about 60° before the dimethyl sulphate is added.

This 4-methyl-3-ethoxy derivative is readily soluble in chloroform and carbon tetrachloride.

1-Phenyl-4-methylurazole.[2]—The above 1-phenyl-3-ethoxy-4-methylurazole was at once hydrolyzed by evaporation to dryness several times with alcoholic hydrochloric acid. This operation should be carried out in a closed tube to prevent loss. The resulting substance was dissolved in alkali, filtered, and precipitated by sulphuric acid. The melting point was 222°–223°. It was extracted in a Soxhlet apparatus with alcohol, but both the portion soluble in alcohol and that left behind melted at the same point as before. This material was used for the quantitative experiments below. Addition of silver nitrate to a solution of the potassium salt precipitates a stable insoluble silver salt.

1-Phenyl-4-methylurazole is difficultly soluble in both cold chloroform and ether. The solubility in water was determined by dissolving a weighed amount of substance in alkali, precipitating with acid, filtering, and weighing. Of 0.1032 gram substance dissolved, in about 75 cc., 0.0891 gram was precipitated, therefore 0.0131 gram remained dissolved. The solubility is then about one part in 5,000 parts of the aqueous filtrate containing small amounts of inorganic substances.

Although the free 4-methyl compound is acid to phenolphthalein, its alkali salts, like those of phenylurazole, are alkaline to methyl orange so that the potassium salts can be titrated quantitatively with a strong acid when the latter indicator is used.

[1] Ber. d. chem. Ges., **36**, 3148 (1903).
[2] *Ibid.*, **36**, 3149 (1903).

I. 0.1032 gram substance required 5.71 cc. 0.0995 N alkali (phenolphthalein) instead of the calculated 5.43 cc. The potassium salt then present required 5.66 cc. 0.0989 N sulphuric acid (methyl orange) instead of 5.45 cc. calculated from the methyl compound or 5.75 cc. from the alkali.

II. 0.1033 gram substance required 5.71 cc. alkali, then 5.69 cc. acid.

1-Phenyl-4-ethylurazole.[1]—Three grams of 1-phenyl-3-ethoxy-urazole were heated with excess of alkali and of ethyl iodide for fifteen hours. After hydrolysis of the ethoxy group by hydrochloric acid a substance was isolated which was readily soluble in ether and chloroform, and could be recrystallized from alcohol. Its melting point was fairly sharp at 168°.5. The amount was too small for further work. As in the case mentioned above, the excess of alkali used decomposed a large part of the material.

1-Phenyl-4-n-propylurazole.—This was prepared like the 4-ethyl derivative above. The substance obtained was purified by recrystallization from alcohol. It melted at 120°, softening at 118°.

0.1160 gram required 5.32 cc. 0.0995 N alkali instead of the calculated 5.29 cc.

Analysis:

0.105 gram substance gave 17.4 cc. nitrogen at 10° and 750.4 mm.

	Calculated for $C_{11}H_{13}O_2N_3$.	Found.
N	19.21	19.57

1-Phenyl-4-n-butylurazole.—This was prepared like the above 4-alkyl derivatives. After hydrolysis by acid, extraction by chloroform, and recrystallization from alcohol, the product melted at 149°–150°, softening at 146°.

0.1130 gram substance required 4.93 cc. 0.0995 N alkali instead of the calculated 4.87 cc.

Only enough material for one analysis was obtained and that, unfortunately, was lost.

1-Phenyl-2-ethyl-4-methylurazole.—This was obtained from

[1] Busch and Heinrichs: Ber. d. chem. Ges., **34**, 2334.

the alkylation process below. The substance obtained from the potassium salt at 60° melted at 51°, softening at 49°. It was found to be easily soluble in ethyl and methyl alcohols, ethyl acetate, ligroin, toluene and acetone. It can be precipitated from methyl alcohol (but not from ethyl alcohol or acetone) by addition of water, and was purified in that way. It then melted at 52°–53°. The analysis is given below on p. 544.

Constant Temperature Bath.

In studying quantitatively the alkylation of the urazole salts it was necessary to have a means of keeping small closed tubes at any desired temperature for a considerable length of time. This has been accomplished by means of a water bath[1] shown in the accompanying figures which was devised and constructed for this purpose. This bath is regulated automatically so that it can be kept at any temperature up to 100° C. as long as desired without variation of more than one- or two tenths of a degree, the change during the alkylation periods being only 0°.01–0°.02.

The bath consists of a tank made of 1.25-inch boards lined with tinned sheet copper, the tinned surface being in contact with the water. This tank is 15 inches deep, 15 wide, and 18 long, and holds, when filled to the usual point, about 45 liters. The cover has the lower side made of tinned copper and fits so neatly that very little steam escapes at 95°. The boards of which any such bath is made should be well oiled before use in order to avoid warping, which is otherwise certain to take place. This tank is surrounded by a layer of cow-hair felt two inches thick and the whole is encased in light boards. This packing insulates the bath so well that at about 90°, if kept closed, it does not cool at a rate of more than 2° per hour.

The bath is heated by means of steam pipes running near the bottom, as shown in Figs. I. and II. These pipes are

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[1] Mr. E. P. Doetsch and Acree have recently developed a bath similar to the one described below, which has a compartment at one end to hold ice. The outside wheel is connected to a shaft running through the side of the bath close to the top; on this shaft is a small brass cog wheel which turns a larger brass cog wheel on the main central shaft. The bath is heated by a flame underneath when higher temperatures are needed. This bath, which will be described in detail later, is much more efficient than the one described here.

of lead, and have thin walls and an internal diameter of one-
half inch. The point at which the steam enters (at *a*, Fig.
I or II) is one inch higher than that (*b*) at which the water
runs out, and the condenser (*c*, Fig. I) slopes as well, so that
there is no chance for water to collect at any place in the sys-
tem. The inner tube of the condenser runs to the bottom of
the steam generator (*e*, Fig. I), so that there is very little loss
of water. The small loss which takes place is compensated
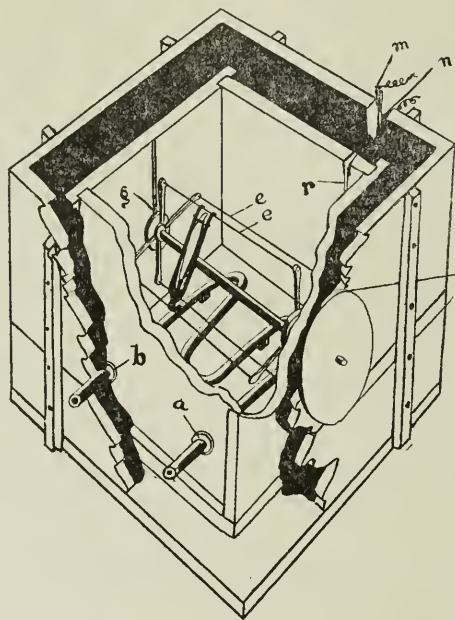
Fig. II.

by the addition of about 300 cc. a week through a tube at (*d*),
Fig. I. A glass water-gauge (not seen in Fig. I) shows the
level of the water in the steam generator. A small detacha-
ble asbestos house, shown in Fig. I, is built around the steam
generator to protect it and the flame. All parts of the con-
denser, as well as the steam supply tube, are made of lead to
avoid any chance of breakage when left running overnight,
and are protected against radiation of heat when necessary.
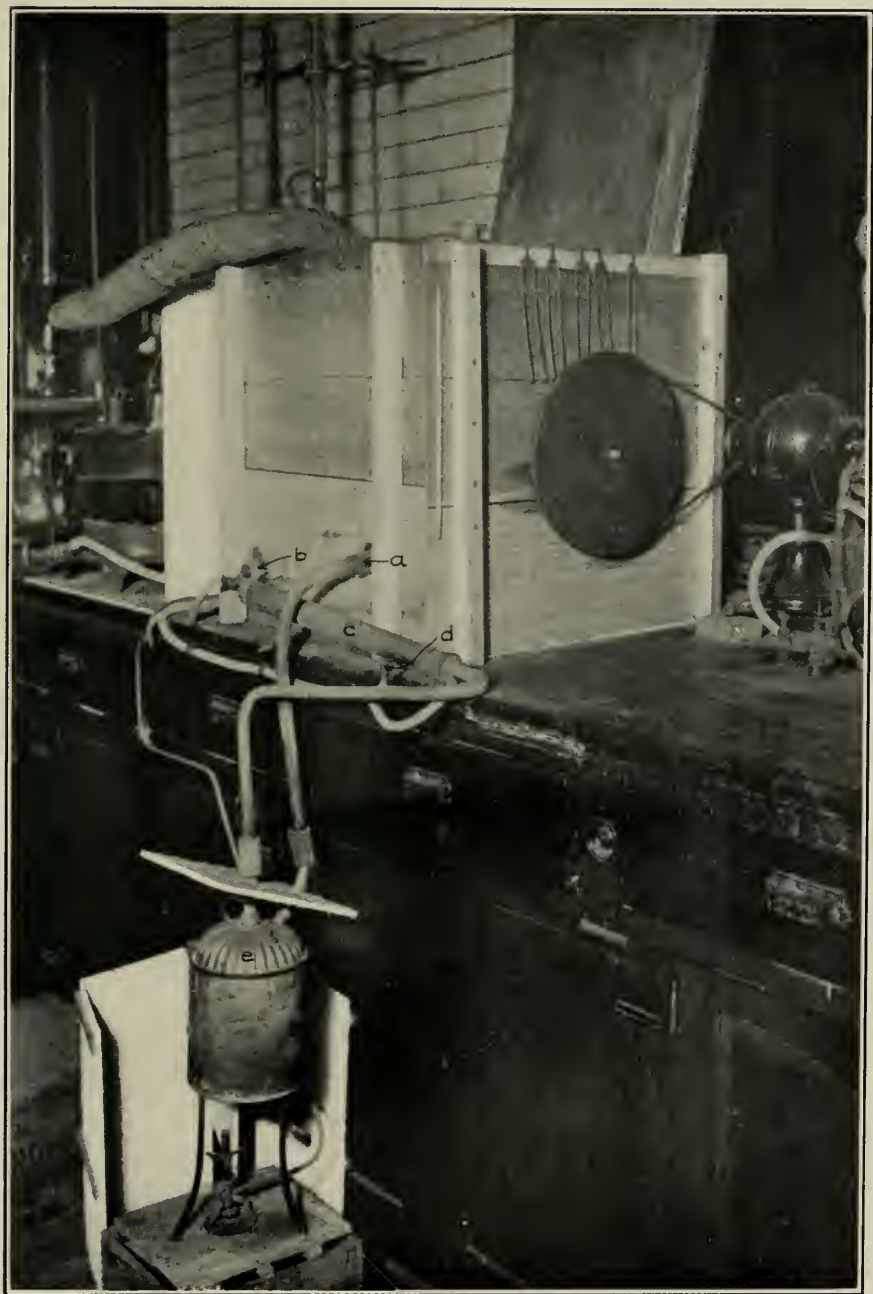
Fig. I.

The tubes running through the walls of the bath have shoulders on the inside, which are fitted with washers and drawn tightly against the side of the tank by collars which screw onto the outer ends. The lead steam pipes are then connected on the inside and outside by means of couplings.

Running through the box is a half-inch brass shaft mounted on bearings as shown in Fig. III. At (c) is a small stuffing box
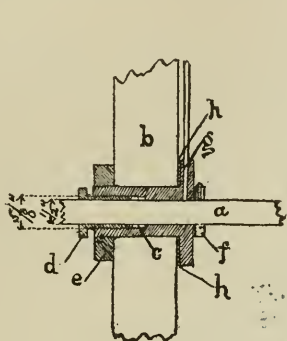
Fig. III.   Fig. IV.

filled with waxed cotton fiber, which is wound round the shaft (a) and jammed in tightly by means of the nut (d) so that the bearing is completely water tight. The shoulder on the inside of the bath is held against a rubber-composition washer (h) by means of the collar (e). The bearing is bored and threaded at (g) and a brass tube introduced, which serves as an oil cup. An oil groove is of course cut on the inside of the bearing.

The shaft carries a framework shown in Fig. II, made completely of brass. The rods (e) are one-eighth inch in diameter and the distance between the diagonally opposite rods is 10 inches. The tubes containing the reagents are attached by fine copper wire to small brass frames similar to that shown in Fig. IV. The sheet brass at (s) furnishes a spring which holds this frame to the brass rods as shown in Fig. II. These frames can be quickly introduced into or removed from the

bath by means of two stout wire hooks. The volume of water is so great that the introduction of a considerable number of tubes at one time does not lower the temperature by a hundredth of a degree. The shaft is kept turning at a rate of 75 to 100 revolutions per minute and both the water and the contents of the tubes are thus kept thoroughly stirred. Flasks or other vessels could be attached to the framework on the shaft without great difficulty.

At first we used at (*r*), Fig. II, a mercury regulator, shaped like that of Reichert except for two bends which allow it to pass out through a slit in the side of the bath. At the binding post (*m*) and the side arm (*n*) electrical connections are made. We have recently, however, discarded this in favor of another form of the Reichert regulator which fits in a hole in a part of the lid which permanently covers the back part of the bath. In this section of the cover there are also two holes for the thermometer. When the mercury touches the point of a platinum wire fastened to one post (*m*), the current passes through a gas regulator of the type devised by Acree, which diminishes the gas supply of the burner under the steam generator, so that the water in the can falls just below the boiling point. When the temperature of the bath again falls, the gas is turned on and in a short time steam is again passing through the pipes. The temperature has been read ordinarily to $0°.01$ with a thermometer graduated to tenths of a degree; and readings taken at intervals over several days, when the bath is not in use and not regulated, have in most cases not varied by more than $0°.1$.

Analytical Method.

In studying quantitatively the rate and products of the alkylation of the salts of 1-phenyl-4-methylurazole, the greatest difficulty was in finding a method of analysis which could be relied upon to give accurate results. It seems desirable to mention some of the difficulties met with, in order that other workers may avoid errors if any changes in the method are necessary.

It was at first thought that a solution of the salt in water

with ethyl iodide, and sufficient alcohol to bring the latter into solution, could be heated in a sealed tube, then analyzed at once by titration of the unalkylated salt present with standard acid and methyl orange. But, although the pure salt requires nearly the theoretical amount of acid, in the presence of the products from the alkylation experiment no definite end point can be obtained, and in some cases compounds seem to be present which decolorize any of the indicators at once.

The next plan was to evaporate the solution to dryness, add water and excess of alkali, and extract with chloroform. But after a few inaccurate results had been obtained it was found that, although an alcoholic solution of the di-N-alkyl derivative can sometimes be evaporated without loss, yet at the temperature of the water bath this substance is appreciably volatile, so that evaporation of a water-alcohol solution is not safe.

It was found, however, that in a solution of 3 cc. water and 2 cc. alcohol the reacting substances would dissolve completely at 60°, and, on washing the tube with 1 cc. more of alcohol and diluting to 50–60 cc. with water, the small amount of alcohol then present would not interfere, as shown quantitatively below, with the complete extraction of the alkylated product. It is also shown below that a chloroform solution of the di-N-alkyl product can be evaporated without loss of material.

The hydrolysis of the O-alkyl product which is present offered more difficulties. This operation was carried out in an open dish until the volatility of one of the substances was discovered. It was then tried in a closed tube with 3–4 cc. concentrated aqueous hydrochloric acid; but the addition of alcohol up to 50 per cent. failed to bring the substances into solution sufficiently to make the reaction complete in four hours at 90°. By using a *saturated* alcoholic solution of hydrochloric acid, however, the hydrolysis could be accomplished in one hour at 90°. If this heating is continued for six or seven hours, some decomposition other than the hydrolysis

appears to take place, giving products insoluble in alkali. Quantitative data on these points are given below.

The method finally adopted is as follows:

Silver Salt.—An amount of the salt equivalent to 15 cc. 0.1 N solution is weighed into a soft glass tube of about 0.5 inch internal diameter, already drawn out at one end to a capillary and sealed. The other end is then drawn out to a long wide capillary so that the capacity of the tube will not exceed the volume of solution to be used by more than one cc. With this precaution the amount of ethyl iodide volatilized into the free space will be less than one per cent. of the amount present and will, therefore, not appreciably affect the results. The solvents desired—water, alcohol, ether— one of them containing in a known volume the desired amount of ethyl iodide, are then introduced from a burette having a long fine capillary attached to its tip. The tube is then sealed and heated. After cooling, the tips of the capillaries are broken off and the contents of the tube and tips washed into a small Soxhlet extraction apparatus with 1–2 cc. alcohol in small portions, and the silver compounds are extracted with ether on the water bath for half an hour. The ether solution is evaporated, the residue transferred to a separating funnel with the help of chloroform, 50–60 cc. water and a slight excess of alkali (phenolphthalein) added, and this solution is extracted four times with 2–3 cc. chloroform. This is evaporated in a weighed porcelain dish and the weight of total alkylated product thus determined. In order to prevent creeping of the chloroform solution during evaporation, it is necessary to keep a gentle current of air, from the breath or by means of bellows, moving across the dish. The dish is removed from the bath just after the chloroform is apparently all driven off, but does not come to constant weight in a vacuum desiccator for five or ten hours, probably on account of traces of chloroform retained. The loss (of chloroform) during this time may be 5–10 milligrams. On cooling, the substance solidifies or can be made to do so by rubbing.

After being weighed it is transferred to a tube closed at one end, the last traces being washed in by 1–2 cc. alcohol, the

tube is drawn out at the other end, 4 cc. alcoholic hydrochloric acid introduced, and the tube is closed and heated for one hour at 90°. It is then cooled and opened, washed with a little alcohol and this[1] solution warmed to 30°–40° in a vacuum desiccator for a short time in order to remove as much of the hydrochloric acid as possible and part of the alcohol. It is then diluted to 50–60 cc. with water, made alkaline, and extracted again with chloroform. Here, as in every case where the solution contains alcohol, each portion of the chloroform used for extraction is run into a second funnel and shaken up with 40–50 cc. of alkaline water to remove any alcohol it may have dissolved. It is then evaporated again in a weighed dish. The residue should consist of the di-*N*-alkylated product. These residues from one series of experiments are united and identified.

Potassium Salt.—As this is soluble in water, the tube to be used is drawn out at both ends at the outset and the salt introduced in a standard aqueous solution. After being heated and cooled, the tube is emptied as above. Only 2 cc. alcohol are used in each tube and 1–2 cc. are sufficient for washing out the solution, so that, after addition of 50–60 cc. water, the alkylated product can at once be extracted by chloroform, with the precautions mentioned above. From this point the procedure is the same as in the case of the silver salt.

Volatility of 1-Phenyl-2-ethyl-4-methylurazole.—The data given below show the loss of the di-*N*-alkyl derivative produced by evaporation with alcohol and aqueous hydrochloric acid, and also by simple heating on the water bath. The first three evaporations with acid were more than sufficient to decompose all of the 3-ethoxy compound present, so subsequent losses must be due to the volatility of the compound in question. The weight given is that of the mixture of di-*N*-alkyl product and 4-methyl derivative remaining in the dish after the evaporation.

I. 0.122 gram = weight after three evaporations.
   0.1075 gram = weight after one more evaporation.
   0.095 gram = weight after one more evaporation.

[1] This procedure is no longer used, the solution being diluted at once with water.

II. 0.186 gram = weight after three evaporations.
    0.1105 gram = weight after one more evaporation.
    0.1065 gram = weight after heating 15 minutes longer.
    0.0970 gram = weight after heating 30 minutes longer.

Evaporation of the chloroform solutions is safe: 0.313 gram substance was dissolved in chloroform and the solution evaporated. The residue weighed 0.310 gram, the loss being 1 per cent. Experiments below give further evidence on this point.

The completeness of hydrolysis of the 3-ethoxy compound in an open dish and the nonvolatility of the 1-phenyl-4-methylurazole are shown by the following experiment: 0.100 gram 1-phenyl-3-ethoxy-4-methylurazole was dissolved in alcohol and evaporated to dryness with addition of aqueous hydrochloric acid three times. The weights of the residues after the successive operations were 0.0855, 0.0855, 0.0855 gram, respectively. The calculated weight was 0.0870 gram, the error being 1.5 per cent.

Extraction of Alkylated Products from Alcohol-Water Solution.—To 1-phenyl-3-ethoxy-4-methylurazole (0.0855 gram) and 1-phenyl-2-ethyl-4-methylurazole (0.0915 gram) were added 60 cc. water and 4 cc. alcohol. The solution was extracted with four portions of chloroform of 2–3 cc. each. After being shaken up with water these were evaporated in a weighed porcelain dish. The weight of the residue was 0.177 gram instead of 0.180 gram, the amount taken at the start.

In another case a solution from which 0.155 gram material had been obtained by four extractions was extracted a fifth time and this last portion of chloroform was evaporated in a separate dish. The substance obtained weighed only 0.0005 gram, showing that the four extractions were sufficient. The solutions were generally extracted four or five times.

Hydrolysis of 1-Phenyl-3-ethoxy-4-methylurazole.—A portion of the compound, weighing 0.179 gram, was heated in a sealed tube with 4 cc. N aqueous hydrochloric acid for 3.5 hours at 91°. All of the substance was recovered (0.201 gram).

A mixture of 3 cc. alcohol and 3 cc. concentrated aqueous acid gave no satisfactory results.

The hydrolysis was found to be complete after heating the material with 4 cc. concentrated alcoholic hydrochloric acid for one hour at 90°. The solution was then made alkaline and any dialkyl body present extracted with chloroform.

I. 0.135 gram ethoxy body was heated with 4 cc. acid. Extraction with chloroform gave a residue of 0.001 gram.

II. 0.1085 gram substance was heated with 4 cc. acid diluted with 1 cc. alcohol. The residue weighed 0.0015 gram.

III. 0.0855 gram ethoxy body and 0.040 gram 2-*N*-ethyl derivative were heated together with 4 cc. acid. 0.042 gram dialkyl derivative was recovered.

IV. 0.104 gram ethoxy body and 0.149 gram 2-*N*-ethyl body were heated with 4 cc. acid diluted with 1 cc. alcohol. 0.1505 gram dialkyl derivative was recovered.

In experiments III and IV, the alkaline solutions, after extraction, were acidified and the precipitate filtered, washed, and dried. It was identified as 1-phenyl-4-methylurazole, melting at 223°.

An attempt was made to determine the amount of *O*-alkyl derivative present in a mixture by hydrolyzing it with gaseous hydrochloric acid and measuring the volume of ethyl chloride formed, but the experiments were not carried far enough to give results that were of any value. The Zeisel method should work beautifully in all these cases, but does not seem to have a great advantage over the above method either in accuracy or convenience. We shall compare these two methods very accurately.

Decomposition of 1-Phenyl-2-ethyl-4-methylurazole by Alkali. —The di-*N*-alkyl compound (0.265 gram) was dissolved in 4 cc. alcohol, 5 cc. 2 N aqueous alkali were added, and the solution was allowed to stand 49 hours. Extraction with chloroform then gave back only 0.0945 gram material. A weakly acid solution can, however, apparently stand several days or longer without decomposition.

In another case about 0.225 gram di-*N*-alkyl derivative, which had been allowed to stand two days with alkali, gave on extraction only 0.1665 gram substance—a loss of 0.060

gram. The mother solution was acidified and again extracted several times, but only 0.022 gram substance was obtained. If the decomposition by alkali were simply a breaking open of the ring between positions 4 and 5, the compound obtained should be soluble in alkali, but precipitated by acids. From the above figures it seems that the decomposition goes further than that.

In general, the analytical method seems to be accurate to about 5 per cent. and this communication is to be judged only from this light. Future work will perhaps enable us to get closer results.

Alkylation Experiments.

1. Among the first experiments, which were carried out before all of the sources of error mentioned above were known and which were therefore rendered inaccurate, a few are interesting as showing roughly the relative rates of alkylation in benzene and alcohol. These experiments were not carried out according to the general method described above. The sodium and silver salts of 1-phenyl-4-methylurazole were used, and the solvent was 12 cc. of either dry alcohol or benzene. The contents of the tubes were evaporated to dryness in open dishes, but, as stated above, the loss probably was not great and would be approximately the same for the two solvents. The column headed "per cent. reacted" gives the percentage of original salt converted into alkylated product. This is easily calculated from the fact that 0.3288 gram would have been the weight of product in each case if the reaction had been complete. The figures for the relative amounts of O- and N-alkylated products are of no value and are omitted. One molecule of ethyl iodide was used in every case.

The potassium salt probably failed to react in benzene on account of its insolubility. The silver salt, however, reacted at 22° three times, and at 51° over four times as fast in benzene as in alcohol. If the difference is due to solubility it must be very great, since the reaction appears to be largely ionic, as shown below, and the alcohol is, of course, the much more strongly ionizing solvent of the two.

Salt used.	Wt. of salt.	Solvent.	Temp.	Time in in hrs.	Wt. prod.	Per cent. reacted.
K	0.344	Benzene	22°	336	0.001	....
K	0.344	Benzene	22°	360	0.001	....
K	0.344	Alcohol	51°	93	0.186	56.6
K	0.344	Benzene	51°	96	0.0025	....
Ag	0.447	Alcohol	22°	240	0.074	22.5
Ag	0.447	Alcohol	22°	241	0.076	23.1
Ag	0.447	Benzene	22°	336	0.1835	55.8
Ag	0.447	Benzene	22°	336	0.1945	59.1
Ag	0.447	Alcohol	51°	93	0.059	18.0
Ag	0.447	Alcohol	51°	93	0.0675	20.5
Ag	0.447	Benzene	51°	96	0.313	95.2
Ag	0.447	Benzene	51°	96	0.304	92.5

2. Alkylation of Potassium 1-Phenyl-4-methylurazole.

All of the experiments below were carried out according to the process described under "Analytical Method."

Standard Solution of Potassium 1-Phenyl-4-methylurazole.— The free urazole derivative (4.779 grams) was neutralized with N potassium hydroxide, 25.04 cc. being required instead of 25.00 cc. calculated, and this solution was diluted to 50 cc. Three cc. then contained 0.344 gram salt and were equal to 15 cc. 0.1 N solution.

Standard Alcoholic Solution of Ethyl Iodide.—Into a 100 cc. flask half filled with absolute alcohol 11.75 grams ethyl iodide were weighed, and the solution was then diluted to the mark and 0.43 cc. more alcohol added. One hundred cc. of solution then contained 11.70 grams ethyl iodide, or 2 cc. contained 0.234 gram and were equivalent to 15 cc. 0.1 N solution. In the experiments described below, each tube contained 3 cc. of the potassium urazole solution and 2 cc. of the ethyl iodide solution.[1] The hydrolysis was carried out in each case by heating one hour at 90° with 4 cc. concentrated alcoholic hydrochloric acid, diluted by 1–2 cc. used in transferring the substances to the tubes.

In the table below, Column III gives the total weight of alkylated product obtained from the chloroform solution

[1] In the recent work a special piece of apparatus, made by Mr. H. C. Robertson, has been used for measuring and transferring the alcoholic solutions without appreciable volatilization of alkyl halide.

used for extraction. If the reaction had been complete this should have been in each case 0.329 gram. After the alkaline solution had been extracted with chloroform the free alkali was neutralized with 0.0989 N sulphuric acid, phenolphthalein being used as indicator. Methyl orange was then added and the unchanged potassium urazole salt present titrated with the same acid. The amount required, measured in cc., is given under V. Since the salt introduced into the tube was equivalent to 15 cc. 0.1 N solution. the part still unalkylated is easily calculated and that value (in per cent.) is given under VI. The sum of the values in IV and VI should obviously be 100.0, but, as stated above, the end point of the titration is not sharp, so that where there is a discrepancy the value in column IV is usually more reliable. Column VII shows what percentage of the total alkylated product contained the entering radical attached to nitrogen:

Table I.—*Potassium Salt at 60°.*

I. No.	II. Time.	III. Total prod.	IV. Per cent. reacted.	V. Acid to titrate.	VI. Per cent. not reacted.	VII. Wt. N ester.	VIII. Per cent. N-ester.
1	30 m.	0.060	18.3	12.70	84.7	0.0585	(97.5)
2	30 m.	0.063	19.2	12.62	84.1	....	...
3	30 m.	0.0545	16.6	12.00	80.0	0.0490	89.9
4	1 h.	0.079	24.0	11.12	74.1	0.075	95.0
5	1 h.	0.1045	31.8	10.37	69.1	0.0935	89.5
6	1 h.	0.095	28.9	10.77	71.8	0.0845	89.0
7	2 h.	0.158	48.05	7.95	53.0	0.144	91.1
8	2 h.	0.159	48.35	8.17	54.5	0.146	91.8
9	4 h.	0.207	63.0	5.85	39.0	0.1815	87.7
10	4 h.	0.206	62.7	5.86	39.1	0.1865	90.5
11	24 h.	0.273	83.0	2.46	16.4	0.2455	89.9

Mean per cent. N-ester about 91.0

The various lots of 1-phenyl-2-ethyl-4-methylurazole obtained in these experiments were united and analyzed without further purification.

Analysis:

0.1405 gram substance gave 23.6 cc. nitrogen at 20°.4 and 753 mm.

	Calculated for $C_{11}H_{13}O_2N_3$.	Found.
N	19.22	19.43

This substance was purified as described on p. 533, and in the following alkylations the 2-4-di-N-alkyl derivative was identified by its melting point.

In the following table the averages of values from Table I have been substituted in the equation for the velocity of a bimolecular reaction, $\dfrac{dx}{dt} = K(A-x)^2$, $\Big($ the initial concentrations, A, of the two substances being the same), which on integration becomes $1/t\ \dfrac{x}{A-x} = A\ K$; A and x are given in gram molecules, the time, t, in hours.

Table II.

I. Time.	II. Per cent. reacted.	III. $A \times 10^4$.	IV. $x \times 10^4$.	V. $(A-x) \times 10^4$.	VI. $A\ K$.
0.5	18.0	15	2.70	12.30	0.439
1.0	30.35	15	4.19	10.81	0.453
2.0	48.2	15	7.23	7.77	0.465
4.0	62.85	15	9.43	5.57	0.423

In the one-hour values that from experiment No. 4 is omitted as it is so much lower than the rest. The sum of the values in columns IV and VI (Table I) would indicate that the analysis of the contents of that tube was correct, so that an error was perhaps made in filling the tube. If this value is averaged in with the others, the value of $A\ K$ is 0.393. If the highest figures for the first two time periods are used, the values for $A\ K$ become 0.461 and 0.466, respectively. The experiment continued for 24 hours is of no value in this connection since the ethyl iodide not used for alkylation was decomposed long before the end of that time.

Two tubes were filled and simply kept at room temperature, which averaged about 22°. The ethyl iodide did not completely dissolve at this temperature, but the tubes were shaken frequently. The quantities of reagents and solvents were the same as in the experiment at 60°.

Table III.—*Potassium Salt at 22°.*

I. No.	II. Time.	III. Total product.	IV. Per cent. reacted.	V. Acid to ti- trate.	VI. Per cent. not reacted.	VII. Wt. N-ester.	VIII. Per cent. N-ester.
12	312 h.	0.1665	50.6	7.5	50.0	0.1555	93.4
13	312 h.	0.1665	50.6	7.5	50.0	0.1600	96.1

Mean per cent. N-ester = 94.8
Melting point of N-ester = 50°–51°

Table IV.—*Potassium Salt at 90°.*

I. No.	II. Time.	III. Total prod.	IV. Per cent. reacted.	V. Acid to titrate.	VI. Per cent. not reacted.	VII. Wt. N-ester.	VIII. Per cent. N-ester.
14	$4^1/_3$ m.	0.0725	22.1	11.25	75.0	0.064	88.3
15	30 m.	0.1945	59.1	4.28	28.5	0.178	91.5
16	15 h.	0.262	79.7	....	....	0.234	89.3

Mean per cent. N-ester = 89.7
Melting point of N-ester = 50°–50°.5

The relative amounts of N- and O-ethyl derivatives found are thus nearly or quite independent of the temperature, although there seems to be a decrease in the per cent. of N-ester as the temperature rises, which will be investigated very closely. Since so few experiments were carried out at 22° and 90°, the results hardly justify the conclusion that there is an appreciable change in the ratio.

3. Alkylation of Silver 1-Phenyl-4-methylurazole.

In the alkylation of the silver salts, since a large amount of solvent must be used for extracting the insoluble residue, ether was used in place of alcohol or water. This also prevented decomposition of the ethyl iodide to any such extent as took place with the other solvents. Each tube contained a weight of silver salt (0.447 gram) equivalent to 15 cc. 0.1 N solution.

Standard Ether Solution of Ethyl Iodide.—A 50 cc. flask was partly filled with ether, weighed, and 3.918 grams ethyl iodide added. The solution was diluted to the mark and 0.22 cc. more ether added. Six cc. of this solution then contained 0.468 gram ethyl iodide, or two molecules for every one of silver salt. Column IV gives the per cent. of *salt* which had reacted in the given time.

Table V.—*Silver Salt at* 60°.

I. No.	II. Time.	III. Total prod.	IV. Per cent. reacted.	V. Wt. N-ester.	VI. Per cent. N-ester.
17	45 m.	0.0505	15.4	0.0215	42.6
18	45 m.	0.0515	15.7	....	....
19	125 m.	0.212	64.5	0.0840	39.6
20	125 m.	0.206	62.6	0.0730	35.4
21	23.5 h.	0.313	95.2	0.117	37.4
22	23.5 h.	0.291	88.5	0.106	36.4
23	96.5 h.	0.300	91.2	0.1125	37.5
24	96.5 h.	0.307	93.4	0.1085	35.4

Mean per cent. N-ester = 37.8
Melting point of N-ester = 48°–49°

Table VI.—*Silver Salt at* 90°.

I. No.	II. Time.	III. Total prod.	IV. Per cent. reacted	V. Wt. N-ester.	VI. Per cent. N-ester.
25	8 m.	0.0800	24.3	0.025	31.3
26	8 m.	0.0855	26.0	0.027	31.6
27	90 m.	0.2985	90.7	0.109	36.5
28	90 m.	0.3165	96.3	0.1105	34.9

Mean per cent. N-ester = 33.6

Experiments with the silver salt at 25° will be carried out in the future. The percentage of N-alkylated product formed at the two temperatures does not vary greatly here, although there is apparently a slight decrease in the per cent. of N-ester with rise in temperature.

Rearrangement Experiments.

The result of these experiments has been to show that 1-phenyl-3-ethoxy-4-methylurazole is not rearranged appreciably into the isomeric 2-N-ethyl derivative under the influence of ethyl iodide at the temperatures at which the above alkylations were carried out, nor does rearrangement take place at higher temperatures as far as tried.

Two tubes were filled with 0.200 gram 1-phenyl-3-ethoxy-4-methylurazole, 2 cc. alcohol, 3 cc. water, and 0.213 gram (1.5 mols.) ethyl iodide, and heated at 90° for 24 hours. They were then opened and the contents treated as in the case of the alkylation of a potassium salt. After hydrolysis the substance insoluble in alkali from each tube weighed 0.002 gram.

A tube similarly filled, except that it contained 9.5 molecules of ethyl iodide, was heated 2 hours at 150°. From this 0.004 gram product insoluble in alkali was obtained.

A last tube, which contained 0.200 gram material, 2 cc. benzene and 0.143 gram (1 mol.) ethyl iodide, was heated an hour at 200°, then an hour at 160°. From this 0.002 gram product insoluble in alkali was obtained.

This small amount of substance did not in any case look like the 2-*N*-ethyl derivative nor did it have the characteristic odor of that substance. It was probably the result of slight decomposition or else was present as impurity at the outset. The ethoxy compound used was not in perfectly pure condition.

The experiments above on the hydrolysis of the ethoxy derivative are also of interest in this connection. A mixture of the 2-*N*-ethyl and 3-ethoxy compounds was heated with alcoholic hydrochloric acid. The results show that neither hydrochloric acid nor the ethyl chloride (formed during the reaction) effects a rearrangement of either compound into the other.

Hydrolysis of Ethyl Iodide.—Potassium phenylurazole and the salt of the 4-methyl derivative undergo some hydrolysis. The potassium hydroxide so formed would decompose ethyl iodide, and water to a less extent produces the same effect. Some action of this sort evidently took place in the alkylation experiments above since the yield of alkylated products stopped increasing after a certain time, although the reaction was not complete. It was desired to make an approximate study of the correction for this decomposition in the reaction above and the plan was to try the action on ethyl iodide of some salt hydrolyzed to about the same extent as the urazole salt used. The compound that we chose for this purpose was potassium carbonate in 0.05 N solution.[1]

As seen, the errors of analysis above are so great that such a correction is not of great value, but the figures for the experiments with the carbonate are of interest.

A standard solution of potassium carbonate was made by

[1] THIS JOURNAL, **29**, 453 (1903).

dissolving 6.92 grams of the salt in water and diluting to 200 cc. Two cc. of solution then contained 0.0692 gram, equivalent to 5 cc. tenth-molecular normal solution, or to 10 cc. of the acid solution called 0.1 N above—that is, one-third of the molecular concentration of the potassium urazole used above. Two cc. of this solution neturalized 9.95, 10.01, 10.03 cc. standard sulphuric acid (methyl orange). The mean is 10.00 cc. Two cc. of the alcoholic ethyl iodide solution of the usual strength were employed.

Each tube contained 0.234 gram ethyl iodide and 0.0692 gram carbonate.

The equation for the reaction velocity is

$$\frac{dx}{dt} = K(A-x)(B-x),$$

and on integration, when $x = 0$ if $t = 0$,

$$1/t \log \frac{B(A-x)}{A(B-x)} = (A-B)K \text{ or } 1/t \ln \frac{B(A-x)}{A(B-x)} =$$

$$0.4343 (A-B)K = (A-B)K'.$$

Let B be the initial concentration of ethyl iodide and A that of potassium atoms. The molecular concentration of potassium carbonate is 5×10^{-4}, but since each molecule of ethyl iodide decomposed into hydriodic acid neutralizes only half a molecule of carbonate, it is better to define A as above, so that x will have the same relation to A and B.

The temperature was 60° and the times taken were the same as in the alkylation of the potassium salt above at that temperature. The time is measured in hours. The titration is given in cc.

Table VII.

$A \times 10^4$.	$B \times 10^4$.	Time.	Titration.	Mean titration.	$x \times 10^4$.	$(A-B)K'$.
10	15	0.5	9.23	9.21	0.79	0.0562
10	15	0.5	9.19			
10	15	1.0	8.54	8.58	1.42	0.0537
10	15	1.0	8.61			
10	15	2.0	7.49	7.49	2.51	0.0543
10	15	2.0	7.48			
10	15	4.0	5.96	5.95	4.05	0.0511
10	15	4.0	5.94			

The above results leave no doubt as to the order of the reaction, but in the present case that indicates nothing as to the mechanism.[1]

A solution of alcohol and water also decomposes ethyl iodide, as shown below. Tubes were filled with 2 cc. alcohol containing 0.234 gram ethyl iodide and 3 cc. water. If the ethyl iodide were all converted into hydriodic acid it would neutralize 15 cc. 0.1 N alkali. The amount of acid present after different intervals was determined by titration.

If the reaction were not reversible, the velocity should apparently depend only on the concentration of the ethyl iodide, since the concentration of the alcohol is about 435×10^{-4} and that of the water 1670×10^{-4}, and the change in either of them is, therefore, inappreciable. The chance of error in the first titrations is of course great. The great variation in the value of K is most probably due to the reversibility of the reaction. We have since obtained a great deal of evidence for this.

The equations are,

$$\frac{dx}{dt} = K (A - x)$$

$$1/t \log \frac{A}{A - x} = K \text{ or } 1/t \ln \frac{A}{A - x} = 0.4343 \, K = K'.$$

The experiments were carried out at 60°. The times are given in minutes.

Table VIII.

Time.	Titration.	$A \times 10^4$.	$x \times 10^4$.	$K' \times 10^3$.
31	0.34	15		
31	0.34	15	0.32	0.30
60	0.38	15		
60	0.42	15	0.40	0.20
120	0.74	15		
120	0.71	15	0.73	0.18
243	1.20	15		
243	1.21	15	1.21	0.15

Alkylation of Potassium 1-Phenyl-3-thiourazole.—A few ex-

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[1] This reaction and that of alkyl halides with alkalies, with phenolates and alcoholates in absolute alcohol, and with urazole salts are being investigated.

periments have been carried out on the action of ethyl iodide on the potassium salt of 1-phenyl-3-thiourazole,[1] formula (I):

$$C_6H_5N - N \qquad\qquad C_6H_5N - N \qquad N = NC_6H_5$$
$$OC \quad C.SH \qquad\qquad OC \quad C-S-SC \quad CO$$
$$NH \qquad\qquad\qquad NH \qquad\qquad NH$$
$$I. \qquad\qquad\qquad\qquad II.$$
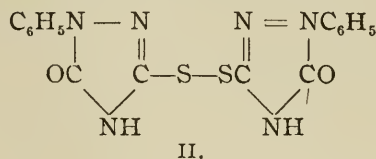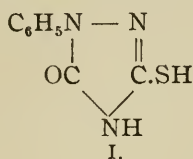
This salt reacts with ethyl iodide in the cold, giving the 3-ethylthio derivative. The thiol group at 3 is so much more strongly acid than the enol group of the oxygen compounds that the metal in the monopotassium salt is probably practically all at 3. Although, from the conclusion reached above, we should expect a small amount of *N*-salt to be present also, the amount of *N*-alkyl product formed is so small as to be negligible, the thio ethyl derivative when first isolated being practically pure. We shall later measure the ratio *N*-ester : *S*-ester given by thio-amides. By using this compound we are thus enabled to study the alkylation at practically one position alone and we hope, by further work, to obtain certain evidence on the question as to whether the alkylation reaction is between molecules or ions. The results already obtained by us and by Dr. F. M. Rogers indicate that both the molecules and the ions are concerned in the reaction.

The course of the reaction is easily followed by titration of the reaction mixture with standard iodine solution, which converts the unchanged salt into a disulphide, formula (II), with formation of potassium iodide. A 0.1 N solution of potassium phenylthiourazole was prepared and 5 cc. were titrated with iodine solution. The results are given in Column II of the following table. Five cc. portions were then mixed with equal volumes of ethyl iodide solution of the same concentration. The solvent in each case was 50 per cent. alcohol. These mixed solutions were allowed to stand at 25° for various lengths of time and titrated. The results of the titration, giving the amounts of unchanged salt, are found in

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[1] Acree: Ber. d. chem. Ges., **36**, 3151 (1903).

Column III. We now have values which can be substituted in the equation for a second order reaction,

$$1/t \frac{x}{A-x} = A K,$$ and the values obtained for $A K$ and K are

given in Columns V and VI:

Table IX.

t.	A.	$A-x$.	x.	$A K$.	K.
10	8.55	6.66	1.89	0.028	0.0033
30	8.55	4.55	4.00	0.029	0.0034
61	8.55	3.22	5.33	0.027	0.0032
120	8.55	1.97	6.58	0.029	0.0034
193	8.55	1.38	7.17	0.029	0.0034
10	9.90	7.51	2.39	0.032	0.0032
13	9.90	6.92	2.98	0.033	0.0033
21	9.90	6.00	3.90	0.031	0.0031
30	9.90	5.13	4.77	0.031	0.0031

In the second series, as is easily seen, a slightly more concentrated solution of urazole salt was used.

Conclusions.

In the above paper evidence has been presented which bears on the general question of tautomerism. The ground has been taken that the great similarity in the behavior of different tautomeric substances and their salts makes it probable that all of the phenomena commonly included under the term tautomerism arise from the same cause. The possible explanations of these phenomena have been discussed and the following conclusions reached:

1. The assumption of different structures for the potassium and silver salts of any tautomeric compound is of no assistance in explaining the reactions of our urazoles, because on careful study both salts are found to behave essentially alike in that mixtures of *N*-ester and *O*-ester are obtained from both.

2. The theory that when a salt gives two isomeric derivatives on alkylation one is an intermediate product in the formation of the other cannot hold in the present case, because (1) neither derivative has been found to rearrange appreciably into

the other, and (2) the ratio of the two products is practically the same at all times during the course of the reaction.

3. It is shown that the "addition theory" does not explain as easily as the theory here advocated the nature of the reaction, and the fact that in a large number of reactions the velocity *decreases* upon the addition of many electrolytes, whereas an *increase* is required by the "addition theory."

4. It is shown that *the assumption of two different salts in equilibrium* will account for all the facts known in connection with our compounds.

5. The salts of phenylurazole were treated with alkyl halides and found to yield in all cases a mixture of *N*-ester and *O*-ester.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD., May 1, 1910.

NOTE ON THE EXPERIMENTAL ILLUSTRATION OF THE LAW OF MULTIPLE PROPORTIONS.

BY J. H. KASTLE.

As a teacher I have frequently experienced the need of a simple, rapid and accurate experiment for illustrating the law of multiple proportions. In looking about for such a method it occurred to me, several years ago, that in cuprous chloride we probably have a substance capable of yielding good results in the experimental illustration of this law. When this compound is gently heated in moist or dry chlorine it is converted quantitatively into anhydrous cupric chloride. The increase in weight obviously gives us the quantity of chlorine with which a given amount of copper combines in passing from the cuprous to the cupric condition and a determination of the copper in the resulting cupric chloride gives us by difference the several amounts of chlorine with which this quantity of copper is combined. I myself have used this method of experimentally illustrating the law of multiple proportions, on the lecture table, with excellent results, and a number of my students have been equally successful with it in their own work. Indeed, I know of no method for the experimental illustration of this important chemical law which in any way

compares with it in rapidity and nicety of result. The ex-
periments were carried out in the following manner:

From 0.1 to 0.25 gram of pure, finely powdered cuprous
chloride, prepared by the usual methods, is accurately weighed
in a small porcelain boat, 1 to 1.5 inches in length, and spread
over the bottom of the boat as evenly and uniformly as possi-
ble. The boat, with its contents, is then placed in a combus-
tion tube, 8 to 9 inches in length, and gently heated over the
free flame of a Bunsen burner to constant weight in a gentle
current of moist or dry chlorine. The chlorine employed in
the following determinations was prepared by the action of
hydrochloric acid on manganese dioxide and was washed by
passing through a small amount of water contained in a Drech-
sel absorption cylinder. In those cases in which dry chlorine
was employed the gas was dried by passing it through concen-
trated sulphuric acid, contained in a Drechsel cylinder inter-
posed between the washing cylinder and the combustion tube
containing the porcelain boat. Under these conditions the
cuprous chloride is rapidly converted into anhydrous cupric
chloride, and with the quantities of cuprous chloride recom-
mended above it has been found that 30 minutes' heating in
the current of chlorine is sufficient to complete the change.
The tube is then allowed to cool somewhat in a slow current
of chlorine and while still warm the boat with its contents is
carefully transferred to a weighing bottle, which is allowed
to cool in a desiccator over sulphuric acid and weighed. The
increase in weight gives the quantity of chlorine which has
been absorbed by the cuprous chloride. The boat is then
heated again for a short time (5 or 10 minutes) in the current
of chlorine and again cooled and weighed. Generally, how-
ever, the gain in weight during the second heating is very
slight, and as a rule a single heating in chlorine gas is sufficient
to insure complete conversion of cuprous into cupric chloride.
Inasmuch as cupric chloride is volatile at high temperatures,
care should be exercised not to heat the tube too hot. If,
however, the experiment be properly carried out, not the
slightest trace of sublimate is visible on the walls of the tube

in which the porcelain boat containing the cuprous chloride is being heated.

After weighing, the anhydrous cupric chloride is dissolved in water and the copper determined, in the usual manner, as metallic copper, either by electrolysis or by precipitation with zinc. In the event that the cuprous chloride has not been completely converted into cupric chloride a residue of the former will remain undissolved when the contents of the boat are dissolved in water. This in itself affords a check on the accuracy of the work. When employed as a lecture-table demonstration, the weighing of the cuprous chloride, its conversion into cupric chloride, and the weighing of the cupric chloride were all accomplished in one hour and the determination of the copper by electrolysis or by precipitation with zinc begun. The determination was completed and the metallic copper weighed in the presence of the class the next day.

The following results were obtained by the writer in the ordinary course of lecture-table demonstrations:

No. of experiment.	Cuprous chloride taken.	Time of heating in chlorine (minutes).	Cupric chloride found.	Copper found.	Chlorine in cuprous chloride.	Chlorine in cupric chloride.	Chlorine ratio.
1	0.0780	30	0.1052	0.0510	0.0270	0.0542	1 : 2.007
2	0.0910	30	0.1240	0.0574	0.0336	0.0666	1 : 1.982
		15	0.1296				
3	0.0958	30	0.1310	0.0610	0.0348	0.0700	1 : 2.011
4	0.2304	30	0.3098	0.1495	0.0809	0.1603	1 : 1.981
5	0.2965	30	0.3885	0.1703	0.1262	0.2182	1 : 1.729

On dissolving the cupric chloride obtained in Exp. 5 in water, a small amount of cuprous chloride was left undissolved, indicating that the conversion of cuprous into cupric chloride had been incomplete. This, of course, accounts for the low chlorine ratio obtained in this particular experiment and also for the fact that the quantity of copper found was considerably less than the calculated amount for the weight

of cuprous chloride taken. It is also evident from Exp. 3 that 30 minutes is sufficient for the complete conversion of small amounts of cuprous chloride into cupric chloride. Omitting Exp. 5, which was clearly demonstrated to be incorrect, the average chlorine ratio for four experiments is 1 : 1.9952. It is evident, therefore, that the conversion of cuprous chloride into cupric chloride, with the determination of the metallic copper contained in the cupric chloride thus obtained, lends itself well to the experimental illustration of the law of multiple proportions. I hope, when the opportunity presents itself, to make a closer study of the effect of temperature and moisture on this process and also of the influence of chlorine carriers.

UNIVERSITY OF VIRGINIA,
March, 1910.

REPORT.

INVESTIGATION OF ELECTROLYTES WITH THE ULTRAMICROSCOPE.

A paper with the above title appeared in a recent issue of the *Physikalische Zeitschrift*, being the first communication to German journals regarding work begun in 1907. The author is J. J. Kossonogow, of Kiew.[1]

The ultramicroscope used was that of Siedentopf and Zsigmondy, and the electrolytes investigated were salts, colloidal silver, and distilled water. The arrangement of the apparatus was as shown in Fig. I:

Fig. I.
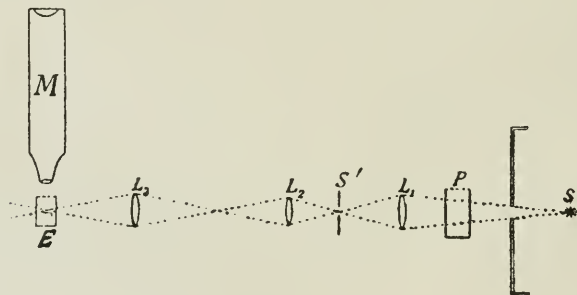
[1] Physik. Z., **10**, 976 (1909). The results of this investigation were communicated to the Physical-Mathematical Society of Kiew, Nov. 5 and 26, 1907, June 2, 1908, and Jan. 26, 1909, and to the Russian Physical Society on Jan. 13, 1909.

The beams of light from the source at S are focused upon the slit S', through which the light diverges and is then condensed to E, where the electrolytic cell is placed. M is the microscope tube, focused upon the layer of liquid illuminated by the narrowest portion of the cone of light. The electrodes were insulated, except at the ends, with caoutchouc, wax and paraffin; their shape is shown in Fig. II. An adjustment on the microscope stand permitted the observer to vary the separation of the electrodes. C is a cover glass protecting the cell.
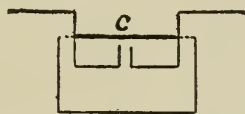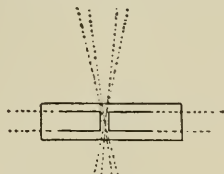
Fig II.   Fig. III.

On viewing the cell through the microscope, flashes of bright light are seen in the field—diffracted light from small particles in the liquid. These execute Brownian movements and often show a linear motion along the path of the light waves. Presumably this motion is due to convection currents, so in front of the first lens is placed a solution of ammonium chloride (P) to serve as a heat filter. The introduction of this solution removes the disturbance.

Photographs of the microscope field are given which are reproduced diagramatically in Fig. IV:
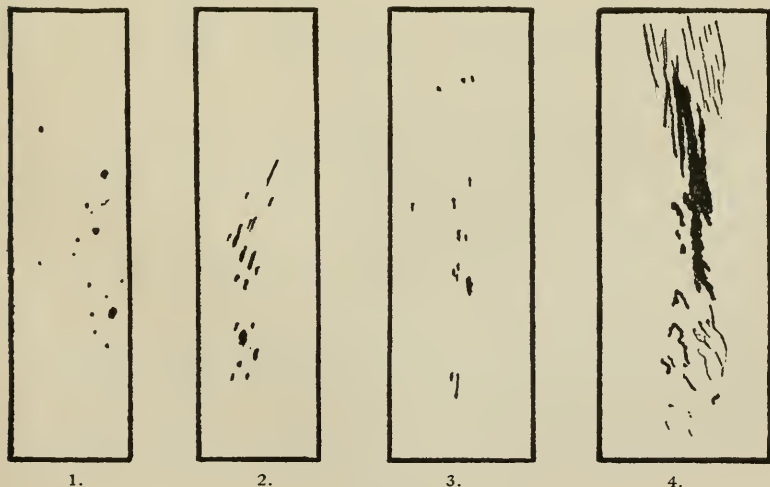
1.   2.   3.   4.
Fig. IV.

(1) and (2) are reproductions of the field when the heat filter is used, (3) and (4) when it is not used.   In the latter pair the influence of convection is very noticeable.   The electrolyte was a 0.01 normal solution of silver nitrate.   Exposures of varying duration are represented.

The condition in the electrolyte as shown in the above diagram changes surprisingly on closing the current circuit. The number of bright points increases enormously, and the points are seen to move in straight lines across the field from anode to cathode.   If the current is reversed, the motion of the particles is reversed also.   Fig. V is a diagrammatic reproduction of a photograph in the original:
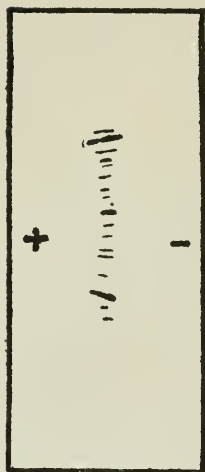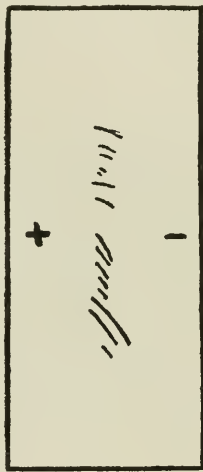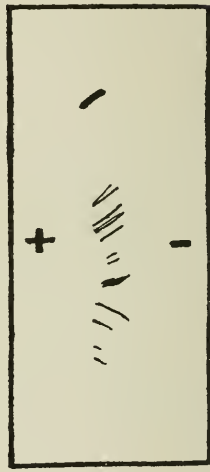
Fig. V.   Fig. VI.   Fig. VII.

The motion is approximately along the lines of force.

A first supposition regarding the nature of the particles observed is that they are dust or other foreign substances suspended in the liquid.   Opposed to this explanation are the following considerations:

(1) During the passage of the current, particles are seen to attach themselves permanently to the cathode surface—products of electrolysis.

(2) The number of points visible increases enormously as the current begins, and does not progressively diminish. It would be supposed that dust particles would presently be swept out, leaving a dark field.

(3) In nonelectrolytes such behavior is never observed.

(4) Ampere's rule is obeyed. When a magnetic field perpendicular to the electrostatic field is excited, the trajectories of the moving particles are bent in a sense corresponding to Ampere's rule. When the magnetic field is reversed, the particles are deflected oppositely (Figs. VI and VII).

Kossonogow considers that the above experiments justify the conclusion that the bright points seen through the ultramicroscope are the representatives of conductors in the electrolyte. Assuming such a relation, he determined the absolute velocities of the points. Being able to observe the movements of an individual point, he noted the time taken for its image to traverse a definite distance on the micrometer scale of the eyepiece, and calculated from the dimensions of the apparatus the actual displacement of the diffracting particle. Velocities determined in this way were of the same order of magnitude as Kohlrausch's ionic velocities.

The foregoing work had to do with electromotive forces considerably higher than the "dissociation potential" of Le Blanc. In order to investigate the phenomena at potentials around that of disssociation, the apparatus shown in Fig. VIII was devised:
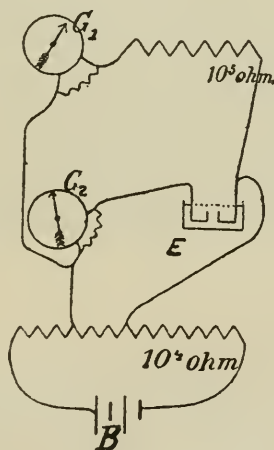
Fig. VIII.

B is a battery having an electromotive force of 8 volts, closed by a resistance of 10,000 ohms, from two points of which the leads to the electrolyte E are brought out. A mirror-galvanometer, G_1, measured the potential applied to the electrodes, while a needle galvanometer, G_2, measured the current

passing. The electromotive force of polarization could be measured by means of G_1, by observing its deflection while connection with B was broken and G_2 was shunted.

Experiments on a 0.01 N water solution of silver nitrate are described. With the battery circuit open, a very few bright points are seen in the ultramicroscope. Under a potential difference of one volt or less, a great number of points are seen, uniformly distributed throughout the field and all moving toward the cathode. At a definite potential, a different condition is observed. A second or so after closing the circuit, a thin dense sheet of particles (10 per 0.001 sq. mm.), in violent vibration, forms close to the cathode. Between this sheet and the cathode surface is a region, 0.05–0.08 mm., absolutely dark. The dark space persists at potentials higher than the critical. In the region between the cathode sheet and the anode is a much less dense distribution of particles, some of which move toward the anode, others toward the cathode. Fig. IX is a diagram of the appearance of the microscope field:
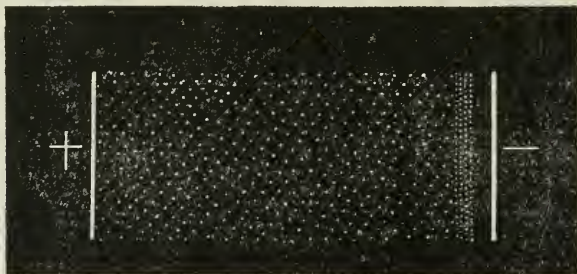
Fig. IX.

The range of values of applied electromotive force through which this phenomenon is observed is very narrow. The "critical potential" is taken as the difference between the applied electromotive force and the electromotive force of polarization of the cell. In one series of measurements on a 0.01 N solution of silver nitrate, with silver electrodes, the critical potential was between 0.988 and 1.049 volts, mean, 1.019. To be sure that this value was independent of the area of the electrode surface, two other measurements were made, with the same separation of electrodes as that used above, but with much greater areas. For these the critical potential was 1.017 and 1.022 volts.

Exactly the same thing was found in the case of copper sulphate, for which the critical potential is a trifle higher than for silver nitrate.

Colloidal silver and ordinary distilled water show also a characteristic appearance at a critical potential, but in these cases the dense sheet forms at the *anode* surface without an intervening dark space. The work on colloidal silver is not described, but the behavior of distilled water is reported in detail.

The characteristic anode sheet appears at potentials which vary with the material of the electrodes. An example is the following:

Electrodes.	Volts.
Ag	1.004
Cu	1.171
Pt	1.769

It is found that the characteristic sheets, both for salts and for distilled water, disappear in one or two minutes after opening the external circuit, and this disappearance is simultaneous with the cessation of the polarization current of the short-circuited cell.

At potentials higher that the critical, say 1.2–1.3 volts, a different arrangement is built up. A great number of bright points are collected at the anode surface, shading off in density toward the cathode. At a point distant from the anode about one-third the total separation of the electrodes is seen a second bright sheet, composed of an enormous number of points. The members of this sheet are in violent agitation, and some seem to depart for the anode, others for the cathode. Further toward the cathode are more points, scattering more and more; in some cases a cathode dark space was observable.

The condition is represented diagrammatically in Fig. X:
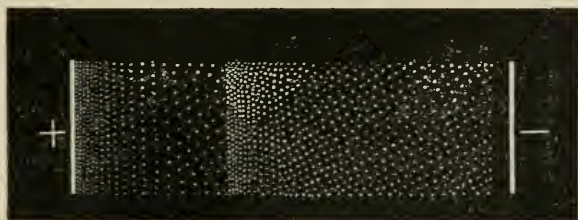
Fig. X.

The effect was found with electrodes of copper, zinc, bismuth, lead and cadmium. Particularly satisfactory results were obtained with lead electrodes.

In the lead cell, laboratory distilled water and commercial lead were used. Immediately after immersion of the electrodes, a number of bright bodies were seen, which in the course of a few hours extended themselves over the whole field between the electrodes. The bodies observed are products of disintegration of the metal.

When a current flows through this cell, at a potential which must exceed a minimum fixed by the electrode separation, the following is observed: Bright particles leave the anode; others, in the neighborhood of the cathode, collect on the surface of that electrode. At a little distance from the positive electrode is a thin sheet of relatively large bright points, parallel to the anode surface and slightly curved toward it at the ends. After this comes a dark region, 0.02–0.04 mm. across, succeeded by a broader strip of very small points, densely packed, and sharply distinguishable from the preceding sheet. The intervening dark space is completely dark when the potential is but slightly greater than the minimum, but at higher potentials points are seen to cross the dark space toward the broad strip, and the sheet curves strongly toward the anode. The appearance of the field changes from that of Fig. XI*a* to that of XI*b*. Kossonogow does not clearly describe the motions of the particles under observation.
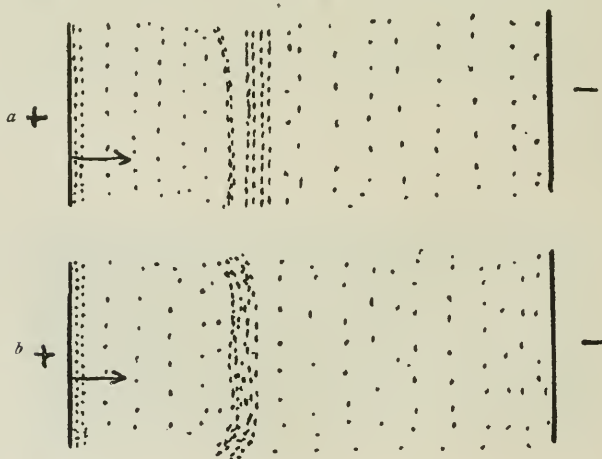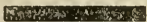
Fig. XI.

The evident significance of the central dark line as separating two regions of different physical character suggested the determination of its position relative to the electrodes. To this end a series of measurements was made, giving a mean value, $d/d' = 11/21$. This, remarkably enough, is nearly the ratio found by Kohlrausch for the relative velocities of hydrogen and hydroxyl ions, *viz.*, $18/33$.

Kossonogow's conclusion, so far as any is drawn, is that the bodies giving rise to the images observed are intimately associated with the conduction of electricity through the electrolyte, of which liquid they are actually a part, and are not dust or foreign matter in suspension.

Criticisms of the work are easy to make, but until a complete account of the investigation is accessible judgment must be reserved. In any event, the paper is highly suggestive. D. MacKenzie.

OBITUARY.

RICHARD ABEGG.

With the untimely death of Abegg, on April 3rd, the new school of Physical Chemistry suffers a severe loss. He was a little over forty-one years old, and, therefore, just in the prime of life.

Abegg was born in Danzig on January 8, 1869. He studied in Kiel, Tübingen, and Berlin, and made the degree of Doctor of Philosophy with A. W. von Hofmann in 1891.

He went to Leipzig to study physical chemistry with Ostwald, and later worked with Arrhenius and Nernst. He was at first an assistant in Nernst's laboratory in Göttingen, in 1894 was appointed privatdozent and in 1898 professor. He went to Breslau in 1899 to Ladenburg's laboratory, and was made Ausserordentlicher Professor in 1900. He remained at the University of Breslau until 1909, when he accepted the professorship of physical chemistry in the Technological High School in Breslau.

The investigations carried out by Abegg covered a very wide field. They were, however, practically all in physical or inorganic chemistry. He was very much interested in the phenomena presented by chemical valence, and contributed not a little to this subject. The problem of complex ions was also studied by him. Abegg's largest work was the editing of a "Handbook of Inorganic Chemistry," which is now only about half completed. Five volumes have appeared, and these place the work among the classics of inorganic

chemistry. As would be expected, his physical chemical training stood him in good stead in editing this book.

Abegg was personally a very attractive man. To one who was a fellow student with him in Ostwald's laboratory, his memory recalls a kind-hearted, genial gentleman, a hard-working, conscientious student and investigator. H. C. J.

REVIEWS.

EXPERIMENTELLE UNTERSUCHUNGEN ÜBER ATOMGEWICHTE. Von THEODORE WILLIAM RICHARDS, Professor an der Harvard Universität, Cambridge (Massachusetts, V. S. A.), und SEINEN MITARBEITERN. 1887–1908. Mit 34 Abbildungen im Text. Deutsche Ausgabe besorgt von J. KOPPEL. Hamburg und Leipzig: Verlag von Leopold Voss. 1909. pp. viii + 890. Price, M. 35.

The following paragraphs are taken from the preface to this book:

"The present volume contains a series of original papers in which are communicated the results of experimental investigations on atomic weights and other related problems which have been carried on in the Chemical Laboratory of Harvard College, Cambridge, in the course of 20 years.

"The direct motive for the publication of this collection in German was furnished by the invitation extended to the author to deliver a series of lectures in the summer of 1907 at Berlin, as a guest of the University, whereby interest in the object of his investigations was naturally increased."

Forty-six papers in all, including three independent communications by Prof. G. P. Baxter, are reproduced in this collection. Prof. Richards's work is too well known to need comment, and this book, thus bringing together into one compact volume the valuable results of his twenty years' work, is a most welcome addition to chemical literature.

C. A. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1909. Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches Appliquées à la Science et à l'Industrie. Par CAMILLE POULENC, Docteur ès Sciences. Avec 172 figures intercalées dans le texte. Paris: J.-B. Baillière et Fils. 1909. pp. viii + 336. Price, Fr. 4.

Former volumes of this annual have already been reviewed in THIS JOURNAL. The first 57 pages of the present book are devoted to physical apparatus, 50 pages are given to apparatus used in ordinary chemical operations, 40 pages to electrical heating devices, etc., 145 pages to apparatus use-

ful for analytical purposes, and 20 pages to bacteriological apparatus.   C. A. R.

THE CALCULATIONS OF GENERAL CHEMISTRY, with Definitions, Explanations and Problems. By WILLIAM J. HALE, PH.D., Assistant Professor of Chemistry in the University of Michigan. New York: D. Van Nostrand Co. 1909. pp. xi + 174. Price, $1.00.

This volume of chemical arithmetic is distinguished from others on the same subject by the careful explanations of chemical and physical laws and by its logical arrangement. For example, the chapter on Avogadro's hypothesis is divided into the following sections, with ample explanation of the problems: the hypothesis, the relation of density to molecular weight, the calculation of relative densities on different standards, the gram-molecular volume and the calculation of densities from molecular weights. Professor Hale's book may be highly commended for use in the first or second year of college work.   E. R.

ANALYSE DES METAUX PAR ÉLECTROLYSE. Par A. HALLARD, Docteur ès Sciences, Chef du Laboratoire Central des Usines de la Cie. Fse. des Métaux, et L. BERTIAUX, Essayeur du Commerce Chimiste à la Cie. Fse. des Métaux. Métaux Industriels, Alliages, Minerais, Produits D'Usines. Deuxième èdition entièrement refondue et augmentèe. Paris: H. Dunod et E. Pinet, Éditeurs. 1909. pp. 253.

This work treats the subject of electroanalysis under four headings: Principles of Analysis, Determination of the Metals, Metals and Metallurgical Products, and Experimental Results. That it meets a need is indicated by the fact that a second edition has been called for, and by the further fact that a German translation has appeared. The various methods are discussed clearly and briefly, and the work as a whole gives evidence of care in its preparation.   H. C. J.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS FROM A PRACTICAL STANDPOINT. By ALFRED J. MOSES, E.M., PH.D., Professor of Mineralogy, Columbia University, and CHARLES LATHROP PARSONS, B.S., Professor of General and Analytical Chemistry, New Hampshire College, Durham, N. H. Fourth edition, with 583 figures. New York: D. Van Nostrand Co. 1909. pp. vii + 444. Price, $2.50.

This work has long been a standard text-book for those desiring a brief course in determinative mineralogy. It has now appeared in a fourth edition, which is essentially the same as the third edition save that the introductory paragraphs to the various chapters have been rewritten and the statistics brought up to date. The book contains a brief, accurate discussion of the subjects of crystallography, blow-

pipe reactions, and determinative mineralogy, with tables for the determination of the common minerals. The illustrations of minerals add interest to the book. It is an excellent work for elementary instruction in mineralogy. C. K. SWARTZ.

LO ZINCO. PROF. ROBERTO MUSU-BOY. Con 10 Incisioni e 4 Tavole. Milano: Ulrico Hoepli. 1909. pp. xiv + 219. Price, L. 3.50.

This is a very interesting monograph on zinc. A brief history of the element is followed by a description of its properties and of its ores, the methods of analysis used to determine the metal and the geological formations in which it occurs. The various metallurgical processes used for its extraction are then described. The locations and general characteristics of the zinc-mining regions of the world and a complete list of the foundries of Europe and America, together with the latest statistics on production, imports, exports, etc., are given, and the manufacture of zinc white is treated at some length. C. A. R.

ENCICLOPEDIA PRACTICA PER LE INDUSTRIE GALVANOPLASTICHE, ELETTROCHIMICHE E FOTOMECCANICHE. P. CONTER. Con 279 Incisioni nel Testo. Milano: Ulrico Hoepli. 1909. pp. viii + 555. Price, L. 5.50.

A compact pocket-size volume containing information, arranged alphabetically, on the substances, apparatus and processes used in the galvanoplastic, electrochemical and photomechanical industries, receipts, first helps to the wounded, etc. The book is copiously illustrated, but each subject is necessarily treated very briefly and, as the author states, this book is intended merely as a *vade mecum* for the busy worker, who has no time to consult more detailed books. C. A. R.

ANLEITUNG ZUM ZWECKMÄSSIGEN RECHNEN BEI CHEMISCHEN PRÄPARATIVEN ARBEITEN. Von E. MOHR. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. pp. 25. Price, M. 0.75.

The author of this booklet points out the many advantages, to the worker, the reader and the learner, of using in all chemical reactions quantities of the reacting substances which are simple multiples of their molecular weights, instead of starting with arbitrary amounts, such as 5, 10 grams, etc. Likewise, he urges that all solutions of reagents be prepared on a gram-molecular basis. Many examples showing the advantages of this system are given. This little book is recommended to the attention of all workers in chemistry, and especially to teachers who have charge of preparation work or who may contemplate writing laboratory manuals. C. A. R.

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American Chemical Journal.

This Journal contains original articles by American chemists; reviews of works relating to chemistry; reports on progress in the various departments of chemistry; and items of general interest to chemists. Twelve numbers of about 100 pages each are published annually, at regular intervals, and form two volumes. A number is issued each month. The subscription price is $5.00 a year in advance; single numbers 50 cents; and foreign subscriptions $5.50 per year in advance; this includes postage.

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